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THIRD EDITION

Peter M. Eller, Ph.D., CIH
Editor

VOLUME 1

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Adherence to exposure control limits has been an important strategy in the prevention of occupational disease for almost 50 years. Methods of monitoring exposure in the occupational environment are vital to this prevention strategy. They produce the information needed to modify and improve control systems so as to protect the worker from occupational health hazards. These methods are also a necessary part of all standards which set limits for environmental exposures to toxic substances.

The methods presented in this improved Third Edition are intended to be accurate, clear and concise. They incorporate the results of recent research by NIOSH. Applicable methods are also incorporated into Criteria Documents produced by NIOSH for recommending standards to the Occupational Safety and Health Administration.

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FOREWORD

Adherence to exposure control limits has been an important strategy in the prevention of occupational disease for almost 50 years. Methods of monitoring exposure in the occupational environment are vital to this prevention strategy. They produce the information needed to modify and improve control systems so as to protect the worker from occupational health hazards. These methods are also a necessary part of all standards which set limits for environmental exposures to toxic substances.

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It is a pleasure to present this Manual for your use and welcome your comments about it.

J. Donald Millar, M.D., D.T.P.H. (Lond.)
Assistant Surgeon General
Director, National Institute for
Occupational Safety and Health
Centers for Disease Control

ABSTRACT

The sampling and measurement methods in the Third Edition of the NIOSH Manual of Analytical Methods are revisions and additions to those contained in the Second Edition, Volumes 1 through 7, published in 1977 through 1981.

This first printing contains 102 revised methods for over 200 toxic substances replacing more than 200 Second Edition methods. Where similarities of sampling and measurement procedures and clarity allowed, the revised methods have been written around groups of substances. The methods are arranged in alphabetical order of method name in two volumes (A through G and H through Z) with separate sections for air, biological, and bulk samples.

Indexes of Names and Synonyms (alphabetical), Third Edition Method Numbers and Second Edition Method Numbers have been included for cross-reference.

Chapters on Quality Assurance, Air Sampling, Development and Evaluation of Methods, and Biological Samples are included.

Additional revised methods will be issued periodically.

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II.	Methods	
	A. Air Samples (A through G in Vol. 1, H through Z in Vol. 2)	

COMPOUND	METHOD NUMBER
Acetic acid	1603
Acetonitrile	1606
Acids, inorganic	7903
Acrolein	2501
Acrylonitrile	1604
Alcohols I (desorption in 99:1 CS_2:2-butanol)	1400
Alcohols II (desorption in 99:1 CS_2:2-propanol)	1401
Alcohols III (desorption in 95:5 CS_2:2-propanol)	1402
Alcohols IV (desorption in 95:5 CH_2Cl_2:methanol)	1403
Aldrin and Lindane	5502
Alkaline dusts	7401
Allyl chloride	1000
Aluminum	7013
Arsenic (hydride AAS)	7900
Arsenic trioxide (graphite AAS)	7901
Benzoyl peroxide	5009
Beryllium	7102
Bromoxynil and Bromoxynil octanoate	5010
2-Butanone	2500
Cadmium	7048
Calcium	7020
Carbaryl	5006
Carbon black	5000
Carbon disulfide	1600
Chlorinated terphenyl	5014
Chloroprene	1002
Chromium	7024
Chromium, hexavalent	7600
Cobalt	7027
Copper (dust and fume)	7029
Cresols	2001
Cyanides (aerosol and gas)	7904

COMPOUND	METHOD NUMBER
2,4-D and 2,4,5-T	5001
sym-Dichloroethyl ether	1004
1,1-Dichloro-1-nitroethane	1601
Dyes, benzidine, o-anisidine, and o-tolidine	5013
Elements (ICP)	7300
Epichlorohydrin	1010
EPN, Malathion, and Parathion	5012
Esters I	1450
Ethylene dibromide	1008
Ethylene glycol	5500
Ethylene thiourea	5011
Fibers (asbestos and others)	7400
Fluorides (aerosol and gas)	7902
Formaldehyde (oxazolidine)	2502
Formaldehyde (chromotropic acid)	3500
Formaldehyde (Girard T)	3501
Hydrazine	3503
Hydrocarbons, BP 36 - 126 °C	1500
Hydrocarbons, aromatic	1501
Hydrocarbons, halogenated	1003
Hydroquinone	5004
Isocyanate group	5505
Isophorone	2508
Kepone	5508
Ketones I (desorption in CS_2)	1300
Ketones II (desorption in 99:1 CS_2:methanol)	1301
Lead	7082
Lead sulfide	7505
Mercury	6000
Methanol	2000
Methylene chloride	1005
Mevinphos (Phosdrin)	2503
Naphthas	1550
Nitrogen dioxide	6700
Nitroglycerin/EGDN	2507
Nitrous oxide	6600
Nuisance dust, total	0500
Nuisance dust, respirable	0600
1-Octanethiol	2510
Paraquat	5003
Phenol	3502
Polychlorobiphenyls	5503
Rotenone	5007
Silica, crystalline (XRD)	7500
Silica, crystalline (color)	7601
Silica, crystalline (IR)	7602
Tetraethyl pyrophosphate (TEPP)	2504
Thiram	5005
Tungsten (soluble/insoluble)	7074
Turpentine	1551
Vinyl bromide	1009

COMPOUND	METHOD NUMBER
Vinyl chloride	1007
Warfarin	5002
Welding and brazing fume	7200
Zinc	7030
Zinc oxide	7502

B. Biological Samples (Vol. 1)

ALAD in blood	8000
Benzidine in urine (TLC)	8304
Benzidine in urine (GC)	8306
2-Butanone, ethanol and toluene in blood	8002
Fluoride in urine	8308
Hippuric acid in urine (color)	8300
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MBOCA in urine	8302
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HOW TO USE

I. INTRODUCTION

A. PURPOSE AND SCOPE

This Manual is a collection of air and biological analytical methods which NIOSH has evaluated. The scientific literature contains equally accurate methods. We plan to augment this Manual in the future with methods developed, evaluated or revised by NIOSH. There will be situations where users of these methods will need to modify them to accommodate interfering compounds from the workplace under investigation, to take advantage of special capabilities of the laboratory or to make possible the analysis of a single sample for several contaminants. For example, in elemental analysis by atomic absorption or emission, filter samples containing relatively high levels of organic particulate matter may require digestion in a larger quantity of acid for a longer period of time. As another example, chromatographic procedures are commonly modified to eliminate interferences by changing the column and conditions and by using a more specific detector. The automation of sample work-up and measurement procedures usually requires some modification of the nonautomated procedure. When solid sorbent samplers are used, the volume of air sampled should be reduced if air contamination from vaporous compounds is relatively high and, in some cases, may be increased if such contamination is relatively low. In any case, data showing the reliability of the method used should be obtained.

These methods are intended to promote accuracy, sensitivity and specificity in the analyses [1] while preserving practicability [2]. Some older methods have been retained or refined with the recognition that many laboratories do not have the newer instruments.

Direct-reading instruments and passive monitors are being used with increasing frequency for evaluating workplace air. Direct-reading methods give the chemist and industrial hygienist the opportunity to perform selected analyses at the work site and take action as necessary. Passive monitors eliminate the need for bulky and expensive air sampling pumps, and are being applied to the sampling of many gases. The laboratory chemist is being presented with requests for more complicated measurements; witness the increasing requests for multiple elemental analyses and the deconvolution of complex mixtures by gas chromatography-mass spectrometry, high pressure liquid chromatography and Fourier transform infrared spectrometry. The demand for increased selectivity, resolving power and reduced analysis turnaround time will continue.

---

[1] Keith, L. H., N. I. McClelland, et al. "Principles of Environmental Analysis," Anal. Chem., 55, 2210-2218 (1983).

[2] Horwitz, W. "Practicability in Regulatory Analytical Chemisty," Anal. Chem., 51, 741A (1979).

B. HOW TO USE THIS MANUAL

1. LOCATING A METHOD:

	Use one of the following:
a. By Method Title (methods are arranged alphabetically in Air, Biological, and Bulk sections of the Manual; some methods are combinations of several compounds)	1. Methods section; or 2. Contents (page v); or 3. Index of Names and Synonyms (page A-27; "yellow pages")
b. By Third Edition Method Number (see the system description below)	Index of Third Edition Method Numbers (page A-11)
c. By Second Edition Method Number (P&CAM or S-numbers from Second Edition of the NIOSH Manual of Analytical Methods)	Index of Second Edition Method Numbers (page A-15)
d. By Chemical Abstracts Service Registry Number (CAS #)	Index of Names and Synonyms (page A-27; "yellow pages")

2. THIRD EDITION METHOD NUMBERING SYSTEM

Substances having the same sampler, sample preparation and measurement technique may be grouped together in one method. Substances are assigned method numbers based on the following system:

AIR SAMPLES:

General:	Method Number
Gas	0001-0499
Aerosol	
Total	0500-0599
Respirable	0600-0699
Open	0700-0999

Organic Compounds:

Gas	
Active Sampling	
Solid Sorbent	
Charcoal, coconut shell	
Halogenated compounds	1000-1299
Ketones	1300-1399
Alcohols	1400-1449
Esters	1450-1499
Hydrocarbons	1500-1549
Mixtures	1550-1599
Other	1600-1999
Silica gel	2000-2499
Other solid sorbents (porous polymer, etc.)	2500-3499

	Method Number
Liquid sorbent	3500-3599
Other (whole air, etc.)	3600-3699
Open (direct-reading, etc.)	3700-3999
Open (passive sampling, etc.)	4000-4999
Aerosol	
Vapor pressure not significant	5000-5499
Vapor pressure significant	5500-5999
Inorganic Substances:	
Gas	
Active sampling	
Solid sorbent	6000-6399
Liquid sorbent	6400-6499
Other (whole air, etc.)	6500-6599
Open (direct-reading, etc.)	6600-6699
Open (passive sampling, etc.)	6700-6999
Aerosol	
Vapor pressure not significant	
Metals by flame AAS (XX is Atomic Number)	70XX
Metals by other AAS	7100-7199
Other	7200-7899
Vapor pressure significant	7900-7999
BIOLOGICAL SAMPLES:	
Blood	8000-8299
Urine	8300-8599
Open	8600-8999
BULK SAMPLES:	9000-9999

3. METHOD FORMAT

The methods consist of three major parts:

a. Summary

The first page of each method is designed to provide a quick summary of essential parameters of sampling and measurement in abbreviated form. Also included are separate estimates of overall and measurement precision, if available. References to other NIOSH-evaluated methods for the substance in this and previous editions of this Manual are also given.

b. Instructions

The second page of each method begins with lists of required reagents and equipment and continues through calculations with step-by-step instructions. The instructions are written for use by experienced industrial hygienists and chemists. In some cases, lengthy instructions for sampler preparation or standardization of stock solutions appear in appendices to the method. Additional instructions relating to sampling and measurement are contained in the chapters on quality assurance and sampling (see pages 7 through 12 and

22 through 28). The nomenclature used in the methods and in the introductory chapters is consistent with the definitions given in the Glossary of Abbreviations, Definitions and Symbols (page A-3).

An important part of the instructions is the section on special precautions which must be observed for the safety of personnel during sampling and measurement.

c. Supporting information

Laboratory and field data, where they exist, relating to the method are summarized in the EVALUATION OF METHOD section and on the summary page, along with pertinent references.

4. USER EXPERIENCE WITH THE METHODS

NIOSH seeks to make these methods useful in industrial hygiene analyses. Therefore, the experience of those people using the methods is important to us. Suggestions for improvement and questions relating to this Manual are welcome and should be directed to the Manual Coordinator. Postcards have been included in this Manual to facilitate this process.

C. QUALITY ASSURANCE

by David L. Smith, CIH, and Michele L. Bolyard, CIH, NIOSH/DPSE

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1. ROLE OF LABORATORY QUALITY ASSURANCE PROGRAM

Analytical data are used to make a variety of decisions. Industrial hygiene analytical data could be used to decide whether a particular chemical agent is present in a workplace atmosphere, whether a hazard to workers' health exists in that atmosphere, or whether a workroom atmosphere complies with applicable standards. It may also be used to support decisions being derived from another experiment. Errors in such analytical data can have a variety of costly effects [1]. The consequences of erroneous data may lead to the wrong decision being made as to whether a non-compliance situation exists. If the analytical results are a part of a larger experiment, perhaps the wrong conclusion might be reached or the results might be uninterpretable. If the presence or absence of a particular agent is erroneously reported, a threat to workers' health may be allowed to continue. It is the role of a laboratory's quality assurance program to provide the necessary safeguards to minimize these occurrences and to provide a means of detecting errors when they do occur. There are many good texts and articles addressing the subject of laboratory quality control [2,3,4,5]. The purpose of this chapter is to address some of the aspects of quality control as they relate to industrial hygiene laboratory quality control.

It must be recognized that no quality assurance program can be designed to fit all laboratories since no two laboratories serve the exact same purpose or operate in exactly the same manner. Each laboratory must design its own operating procedures and quality control practices. The purpose of this chapter, therefore, is not to propose concrete recommendations for implementing a quality assurance program, but rather to present aspects of laboratory quality assurance and quality control which should be considered and addressed when designing or reviewing a particular laboratory's quality assurance program.

A successful quality assurance effort cannot be achieved through the efforts of only one individual. A laboratory's quality assurance coordinator needs the assistance and cooperation of all laboratory personnel to be effective. To achieve this cooperation, it is necessary to discourage adversarial relationships between quality control personnel and bench chemists. Analysts must be trained and made aware of the purpose and value of quality assurance functions and, in turn, the quality assurance program must be designed so that its functions are based on sound goals directed toward improving the performance of both the individual analyst and the laboratory as a whole.

Frequently, analytical results are challenged months or years after the analysis is complete. In order to support the original data, an effective, complete, record-keeping system must be maintained. Another chemist must be able to reconstruct the exact treatment to which the samples were subjected solely from a laboratory's records. Furthermore, if the appropriate quality control checks were performed with the analysis and documented, there can be no doubt regarding the results.

2. ORGANIZATION

A laboratory, just as any other organization, should have a clearly defined organizational structure [2]. Responsibilities of each member of the laboratory staff should be in writing and understood by all. In this way, confusion regarding tasks which need to be performed can be avoided.

The specific organizational structure of the laboratory will vary, depending on that laboratory's function. Two functions which relate to quality assurance should be assigned in every laboratory: the quality control coordinator and the sample clerk. The size and nature of the laboratory may preclude assignment of a full-time position to these functions; however, a laboratory member should be assigned these duties and it should be understood that they are to have top priority.

The quality assurance coordinator's functions will depend on the size and nature of the laboratory. This professional has overall responsibility for assuring that reported data meet established standards for precision and accuracy and that these results can be supported scientifically by the various quality control checks performed with the analysis. One of the major functions of this individual is to perform audits of the quality control system and to implement changes that eliminate recurring errors. The quality assurance coordinator should not be under the direct supervision of management responsible for day-to-day laboratory operation. In this way, conflicts between the laboratory's dual responsibilities of providing analytical results in a rapid fashion while maintaining quality can be avoided. The quality assurance coordinator should also serve as a resource person for chemists or managers on questions or problems related to quality assurance and should have a working knowledge of statistics, including quality control charting, and experimental design.

The sample clerk's functions will also vary, depending on the size and function of the laboratory. As a minimum, the sample clerk is responsible for the receipt and log-in of samples. Field samples should be stored in a secure location under proper conditions (temperature, etc.) until analysis. Logging and tracking of

samples in the laboratory is important so that the history of these samples can be documented and processed in a timely manner. The sample clerk may also be given the responsibility of maintaining chain of custody documentation.

3. QUALITY ASSURANCE IN SAMPLING (also see pages 22 through 27)

Quality assurance procedures should not be overlooked by personnel performing field sampling. The field sampling parameters often have more effect on precision and accuracy of the final result than parameters of the measurement [6,7]. Field personnel should attempt to become familiar with sampling and measurement methods which they will use. The methods usually specify the proper sampling media to be used, the correct flow rate and sample volume, as well as special precautions on sample handling, shipping and possible interferences.

Sampling equipment must be maintained in reliable working order. It is desirable to have one person or group given responsibility for the care, maintenance and stocking of field sampling equipment. This person or group should periodically inspect and repair all equipment and keep track of the use and location of sampling equipment when it is signed out. Sampling pumps should be calibrated with each use. This calibration should be performed with the sampler in line. Since differences in pressure drop across the sampler will affect flow rate, it may be necessary to perform the calibration with the actual sampler to be used.

The exact sampling time must be known in order to accurately estimate the sampled volume. Recording only the start and stop time assumes that the pump functions properly over the entire sampling period. Occasional spot checks for proper operation should be made throughout the sampling period.

Since many modern analytical techniques are extremely sensitive, special care must be taken to avoid contamination of field samples [8]. Samples must not be stored or shipped with bulk materials which might spill or otherwise present the possibility for contamination. The glassware or other containers used in sampling and shipping should be subjected to any cleaning procedures recommended in the analytical method.

Careful record keeping in the field is also important. Pertinent information such as temperature, humidity, possible interfering compounds, sampling location, etc. should be documented. Special care should be taken in sample labelling and in preparation of paperwork accompanying the samples so that confusion in the laboratory is avoided.

Field blanks are used to estimate contamination which may occur immediately before and after sampling, during shipment, or while awaiting measurement in the laboratory. The nature and number of blanks taken will depend on the method and sampling situation; therefore, field sampling personnel must attempt to determine what sources of contamination are possible in the specific situation at hand. The field blank strategy must then be designed accordingly. Where possible, a written sample protocol should be developed before actual sampling begins [9,10]. The protocol should contain a description of the environment being sampled; the assumptions made in derivation of the model of that environment; when, where, and how the sampling will be done; and how many samples will be taken. Samplers should be identified by batch or lot number of sampling media.

4. QUALITY ASSURANCE IN MEASUREMENT

Certain quality control checks should be performed with each sample set [5] to further support the reported results on actual field samples. The exact number and nature of these checks depend on the specific method and circumstances under consideration and should be thought of as an integral part of the method itself (i.e., a measurement should not be considered completed without the quality control checks also being completed). Each chemist must take an independent responsibility for assuring that the analytical quality control system works. This can be accomplished by using known spiked samples which closely simulate field samples with regard to concentration and interferences. Since the analyst is most familiar with the methods being used and should know what range in recoveries to expect, problems with the system can be detected early. We will attempt to recommend specific quality control checks to be performed with the methods in this Manual; however, our recommendations cannot be expected to cover all situations. The user of these methods should consider adding additional quality control checks as appropriate.

a. Methods

First, and perhaps most important in the area of quality control, a laboratory must have adequate measurement procedures. These methods should be written so that there is no doubt in the analyst's mind of the exact steps which must be performed and so that future references to the work can be as exact as possible. The methods used should be evaluated, where possible (either by the laboratory itself or by some other organization), to verify that the methods perform satisfactorily. Factors which could be evaluated include the recovery of the analyte of interest from both spiked samples and generated samples, the stability of collected samples or possible interferences to accurate use of the method. Methods should be tested for ruggedness so that critical steps in the analysis can be identified. Experimental designs have been published which permit rapid evaluation of a number of factors involved in the analysis (e.g., [11]).

b. Standards

Standard solutions may be for either identification or quantitation of the analyte of interest. The bulk material used for preparation of standards should be of sufficient purity to avoid errors in the identification or quantitation. Where available, Standard Reference Materials (SRM's available from the U.S. National Bureau of Standards) or other well-characterized standards are useful for assuring that results are consistent with other organizations and agencies. Laboratory reagents and standards should also be properly labelled with contents, receipt and expiration dates.

For quantitation, sufficient numbers of standards should be prepared so that adequate confidence intervals on reported values can be obtained [12]. As a guideline, we recommend that calibration curves be prepared with triplicate points at each of at least five different concentration levels. The standard curve should be prepared so that linearity can be assured over the range of the curve. Also, it is important that the concentration of standard solutions be chosen to bracket the actual samples. In this way, extrapolation outside

the range of standards is avoided. The concentration of standard solutions should be chosen to be consistent with the purpose of the sampling. That is, if it is desired to demonstrate whether exposure standards are being met, then the standard curve should be constructed to bracket the concentrations which would be encountered at or near the applicable exposure standard. If it is desired to demonstrate whether a compound is present in the atmosphere being sampled, then the calibration curve should be constructed closer to the limit of detection. During measurement, working standards should be interspersed with field samples. In this way, it should be possible to detect if instrument drift becomes significant. Internal standards are useful for correcting instrument response for the actual amount of sample injected into a chromatograph. The internal standard should be chosen so that its retention time is reasonably close, but without peak overlap, to the peak of interest.

c. Blanks (also see pages 20 through 21)

A particular analysis may involve several types of "blank" measurements including reagent blanks, media blanks or field blanks. Reagent blanks measure the signal contribution from solvents, acids or other reagents used by the laboratory in preparing samples for analysis. Media blanks measure the signal contribution from the collection media (impinger solution, filter, sorbent tube, etc.) and field blanks measure signal contribution of the media plus any contamination which may have occurred during handling, shipping and storage before analysis. The nature and number of blank measurements will depend on the method and circumstances, but the purpose of all blank measurements is to help prevent errors in identification and quantitation of field samples.

d. Blind Samples

Blind samples are prepared by someone other than the chemist performing the measurement and are to provide an independent check on the accuracy and precision of the measurement.

If blind samples cannot be prepared with confidence, their use should be avoided. In these cases, confusion may result when discrepancies occur and it will not be possible to say for certain whether the measurement or the blind sample was in error.

The results should be used in conjunction with control charting techniques to identify errors or malfunctions in the system [13]. To accomplish this goal, quality assurance personnel should work closely with laboratory personnel to quickly identify and eliminate trouble spots.

It will not always be possible to isolate the source of error in the results of a blind sample. In these instances, it should be recognized that it will not be possible to defend quantitative results for that particular sample set; therefore, reporting of results where these discrepancies occur should be avoided.

e. Recovery Studies

Recovery studies should be performed as a part of the measurement whenever the analyte of interest must be liberated or separated from the sampling media. The analyte of interest should be added to the media at levels consistent with the field samples. These "spiked" samples should then be treated in the same manner as the field samples. Corrections for recovery should be made whenever the measured recovery is significantly different from 100%. Even if recovery has historically been 100%, recovery studies can be useful as additional analytical and calculation checks. It is often helpful for a laboratory to maintain a record of past recovery studies so that current data may be compared for discrepancies.

f. Duplicates

Duplicate preparations of bulk materials are useful as an indication of the uniformity of the bulk material. Duplicate injections or measurements from air samples are of lesser importance since preparations from air samples are generally fairly uniform in nature. True duplicates of air samples are useful as an indication of both the reproducibility of the entire sampling and measurement method and as an indication of the uniformity of the atmosphere being sampled.

5. INTERLABORATORY TESTING

Assignable analytical uncertainty can be considered as consisting of interlaboratory and intralaboratory variability. A knowledge of the magnitude of these two sources of variability is essential in order to interpret and use analytical data properly [14]. Interlaboratory variability can be estimated from the results of analysis of blind samples; however, intralaboratory testing requires the cooperation and coordination of a number of independent laboratories.

Detailed collaborative testing protocols have been proposed [11] and used to evaluate many measurement methods, as well as several industrial hygiene sampling and measurement methods.

Interlaboratory testing can also be useful for defining the relationship of data reported by different laboratories using either the same or different measurement techniques [15]. Participation in such studies can be useful for uncovering errors in methodology or identifying critical steps in the procedures.

The Proficiency Analytical Testing (PAT) Program operated by NIOSH is useful for measuring a laboratory's performance on a variety of common industrial hygiene samples, including solvent vapors on charcoal tubes and metals, asbestos and silica on filters. Participation in this program by laboratories performing industrial hygiene analysis is strongly encouraged.

Similarly, the American Industrial Hygiene Association (AIHA) operates a laboratory accreditation program for industrial hygiene laboratories. Site visits and application reviews can provide a useful review of a laboratory's overall quality assurance system, as well as the adequacy of personnel, facilities and equipment.

6. REPORTING

The detail and nature of the analytical report will depend on the function of the laboratory. As a minimum, the report should include a description or reference to the method used, any deviations or special circumstances encountered with the sample set, estimates of the limits of detection and quantitation, as well as the results themselves. The report should be signed by the analyst and anyone else who is responsible for approving the report. The laboratory should adopt a standard report format and attempt to maintain that format with all reports.

The limit of detection is defined as the amount of the analyte which can be distinguished from background. The limit of quantitation is that amount of analyte above which the precision of the reported results is better than a specified level. There are numerous methods of determining these quantities and many opinions as to which method is correct [4,16,17,18]; nevertheless, the laboratory should decide on a method for determining these quantities and be consistent to the extent possible in its use.

Sample data should be corrected for recovery or desorption efficiency and for reagent and media blank response. However, field blanks should be treated like field samples (corrected for media blanks and recovery). If correction for contamination is necessary, this correction should be performed by the person who submitted the sample.

Data should be reported simply and concisely and in a manner that "their meaning is not distorted by the reporting process [4]." Attention should be given to the number of significant figures reported. Generally, only the last figure reported should be in doubt.

7. LABORATORY NOTEBOOKS

Laboratory notebooks are used for recording all experimental and analytical notes and data [19]. New notebooks should be logged out to a chemist. The notebook remains the property of the laboratory and should be kept in a central location by the laboratory after it is filled.

Notebooks used in the laboratory should be hard-covered and bound. Use of notebooks with removable pages (e.g., loose-leaf notebooks) should be discouraged. The pages of the notebook should be numbered and any entries made by an individual other than that to whom the book was assigned should be noted. Some laboratories require that the individual notebook pages be signed by the chemist for legal reasons.

The notebook should contain all information gathered by the chemist pertaining to the sample. Where appropriate, lab number, field number, sequence number and other identifying numbers are noted. Measurements requested, identification of the method, modifications to the method and the sample originator should be included. A description of the sample (whether bulk material, charcoal tube, etc.) should be included. Data on quality assurance aspects of the the sample set such as blank values, recovery studies and duplicate determinations should also be included. Formulae used to calculate results and a sample calculation should be shown.

If permanent retention of computer printouts, recorder charts or similar items is deemed necessary, they should be pasted, taped or stapled in the notebook, if practical.

The minimum data entered in the notebook should be sufficient to enable another chemist to derive the same results as the original worker, with no other source of information. In addition to this minimum data, any other facts appropriate and pertinent to the sample analysis are to be entered.

A chemist's notebook is always subject to inspection by his colleagues, supervisors or inspectors from outside the laboratory. Therefore, it is imperative that the notebook be maintained in a professional manner and contain all pertinent information that may be required by other parties, regardless of the particular importance of that information to the chemist. Furthermore, the notebook must be maintained in such a manner that it can withstand challenges as to the validity, accuracy or legibility of its contents.

8. INSTRUMENT MAINTENANCE

Laboratory instrumentation must be maintained in proper operating condition. We have found that in numerous cases the cause for out-of-control quality control samples has been traced to faulty instrument performance. In many of these instances, the operator was unaware that instrument performance had degraded. Performance checks can be useful in documenting instrument performance over time and in detecting deviations. To be of use, performance check procedures should be as quick and easy to perform as possible.

An instrument's maintenance history is often valuable in troubleshooting problems with that instrument. The record of instrument maintenance should be maintained in an "instrument logbook" and kept near that instrument or in a recognized location.

Where appropriate (i.e., balances), periodic calibration should be performed and documented. Records of calibration should be recorded in the logbook for that instrument.

Service contracts or maintenance agreements for instrument repair are useful for assuring that instrumentation is serviced by qualified personnel and maintained in proper operating condition.

9. SAMPLE TRACKING

A laboratory should have a mechanism for logging and tracking samples after they are received in the laboratory so that all samples can be processed in the most efficient manner. The exact system used for sample tracking will depend on the size and nature of the laboratory and may range from hand-entry logbooks to sophisticated computer-based systems. The system should include a means of cross-referencing laboratory sample numbers with field sample numbers and it should be possible to determine the chemist, instrument, and other aspects of the sample set from the field number.

Sample tracking systems may also be used to produce management statistics which may aid in forecasting future sample loads or point to problem areas in sample turn-around.

10. QUALITY ASSURANCE RECORDS

Maintenance of quality assurance records aids in recalling details of a particular analysis at a future date. A condensation of quality assurance data can be used as supporting evidence to field personnel should the need arise. Quality assurance records can also be used to track various quality assurance parameters over time (such as desorption efficiency or blank values).

Computerized record-keeping systems should be backed up periodically. Archive copies of computer data require specialized storage conditions and these archive copies may not be reliable for extended periods of time.

Filing of records should be current and accurate. If rapid retrieval of data is not possible, then maintenance of quality assurance records loses its purpose. The primary purpose is to provide a system to furnish information rapidly regarding the status of specific sample sets.

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D. GENERAL CONSIDERATIONS FOR SAMPLING AIRBORNE CONTAMINANTS

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1. CHOOSING MEASUREMENT METHODS AND SAMPLING MEDIA

As proper advance planning minimizes sampling and measurement costs and labor and contributes to a smooth, successful survey, many things must be considered before collecting field samples. The first step is to define sampling objectives. These may include documenting exposures in particular work settings, determining compliance/non-compliance with existing Federal or local standards or recommended exposure limits, or trying to determine the source of a problem. Sampling parameters that should be defined might include type of sample (area vs. personal), contaminant(s) to be sampled, duration of samples, potential interferences and expected contaminant concentrations (or contaminant concentration of interest). Once these parameters are defined, then the proper analytical method and sampling media can be selected. Other general information needed to plan a survey properly include the number of employees, the sampling strategy plan (discussed later), process flow diagram, material safety data sheets on all process materials, the physical states of the substances to be sampled, and potential hazards involved in collecting and shipping the samples.

It is essential to consult with the analytical laboratory before sampling to ensure that the measurement methods available can meet the defined sampling needs. This step should be an early part of survey planning. The laboratory can also assist in choosing sampling media which are compatible with the sampling needs and the measurement methods available. The APPLICABILITY section of the individual methods in this Manual can be helpful in choosing which of the available methods is best for a particular situation.

Whether through consultation with the laboratory or through reading the specific measurement method, the sampling media will be specifically identified, e.g., pore size and type of filter, concentration and amount of liquid media required, and specific type and amount of solid sorbent (see Tables 1 and 2 for common types, characteristics and behavior of solid sorbents). If specific brand name products are called for, no substitutions should be made. Most sampling media are well defined through research and testing; deviations from specifications are

undesirable. For example, most organic contaminants are sampled with a dual section tube containing 100 mg front and 50 mg backup sections of 20/40 mesh activated coconut shell charcoal. If larger mesh charcoal or a different type of charcoal were to be used, the sampling capacity and recovery efficiencies for the contaminant of interest might change from that which is specified in the method.

The physical state of the contaminant(s) being sampled may also be a factor in determining the media required. In the case of polyaromatic hydrocarbons (PAHs), for example, the proper sampler consists of a membrane filter to trap particulate matter and a solid sorbent tube to trap the vapors of certain PAHs so that total collection is assured.

Table 1. Types and uses of solid sorbents.*

Solid Sorbent	Characteristics
Activated charcoal	By far the most commonly used solid sorbent. Very large surface area:wt. ratio. Reactive surface. High adsorptive capacity. This surface reactivity means that activated charcoal is not useful for sampling various classes of reactive compounds (e.g., mercaptans, aldehydes) due to poor desorption efficiency. The high capacity, however, makes it the sorbent of choice for those compounds which are stable enough to be collected and recovered in high yield. Breakthrough capacity is a function of type (source) of the charcoal, its particle size and packing configuration in the sorbent bed.
Silica gel	Less reactive than charcoal. Due to its polar nature, it is hygroscopic and shows a sharp decrease in breakthrough capacity with increasing humidity.
Porous polymers	Lower surface area and much less reactive surface than charcoal. Adsorptive capacity is, therefore, generally lower, but reactivity is much lower as well.
Ambersorbs	Properties midway between charcoal and porous polymers.
Coated sorbents	One of the sorbents upon which a layer of a reagent has been deposited. The adsorptive capacity of such systems usually approaches the capacity of the reagent to react with the particular analyte.
Molecular sieves	Zeolites and carbon molecular sieves which retain adsorbed species according to their molecular size. The limiting factor is that the water molecule is of similar size to many small organic compounds and is usually many orders of magnitude higher in concentration than the species of interest. This unfavorable situation may result in the displacement of the analyte by water molecules. Drying tubes may be used during sampling to eliminate the effects of humidity [1].

*NOTE: Solid sorbents are used for the collection of vapors only. Aerosols are not collected effectively by most sorbent beds, but may be collected by other components of the sampler (e.g., a prefilter, or the glass wool plugs used to hold the sorbent bed in place).

Table 2. Factors affecting the collection behavior of solid sorbents.

Factor	Effects
Temperature	Since all adsorption is exothermic, adsorption is reduced at higher temperatures. Additionally, if there is a reaction between an adsorbed species and the surface or between two or more adsorbed species (e.g., hydrolysis or polymerization), the rate of such reactions increases at higher temperatures.
Humidity*	Water vapor is adsorbed by polar sorbents; their breakthrough capacity for the chemical species is thereby reduced. This effect varies from a substantial one for more polar sorbents, such as charcoal and silica gel, to a smaller one for Ambersorbs and porous polymers.
Sampling flow rate*	Breakthrough volume of a solid sorbent bed tends to be smaller at higher sampling flow rates, particularly for coated solid sorbents. For sorbents such as charcoal whose breakthrough capacity is significantly reduced by high humidity, lower sampling flow rates may actually result in smaller breakthrough volumes [2].
Concentration*	Breakthrough capacity of solid sorbent bed increases (but breakthrough volume decreases) as the concentration of contaminant in air increases [2].

*NOTE: It is important to distinguish between equilibrium (saturation) adsorptive capacity and kinetic (breakthrough) adsorptive capacity of the solid sorbent. The breakthrough capacity is the important characteristic in actual sampling situations. Breakthrough capacity may be significantly affected by sampling flow rate and relative humidity of the air being sampled and may be significantly less than saturation capacity, which is not dependent on sampling flow rate or relative humidity [3].

The sampling pump used to collect the sample must also be compatible with the sampling needs and the media used. Specifically, the pump must be capable of maintaining the desired flow rate over the time period needed using the sampling media specified. Some pumps may not be able to handle the large pressure drop of the media. This will be true for fine mesh (smaller than 40 mesh) solid sorbent tubes, small pore size filters or when attempting to take a short-term sample on a sorbent tube of a higher than normal pressure drop at a flow rate of 1 L/min or greater. As a rule of thumb, all high flow pumps (1 to 4 L/min) can handle at least 3 kPa (12 inches of water) pressure drop at 1 L/min for 8 hrs. Some pumps can handle up to 7.5 kPa (30 inches of water) pressure drop at flows up to 2 or 3 L/min. Most low flow pumps (0.01 to 0.2 L/min) can handle the pressure drops of available sorbent tubes without problems except that the nominal flow rate may decrease for certain models. All pumps should be calibrated with representative sampling media prior to use. It is good practice to check the pump calibration before and after use each day. As a minimum, calibration should be done before and after each survey.

2. FIGURING SAMPLING PARAMETERS

Once the sampling media and measurement method are chosen, then the specific sampling parameters need to be determined. For most methods, this will not pose a problem as the flow rate recommended in the method can be used for the desired sampling period, e.g., 1 to 3 L/min for 8 hrs for most aerosols or 10 to 200 mL/min for 8 hrs for most sorbent tube samples. Generally, the parameters which must be considered are flow rate, total sample volume, sampling time (tied into the two previous parameters), and limit of quantitation (LOQ) (see Glossary of Abbreviations, Definitions and Symbols). Some of these variables will be fixed by sampling needs, e.g., sampling time or by the measurement method of choice (LOQ or maximum sampling volumes). The choice of these variables can best be explained through the use of the following examples.

Examples:

1. Sampling for Gases and Vapors Using Solid Sorbents

Given parameters:	Method 1501 for Styrene
Recommended Sample Volume:	5 L
Useful Range of the Method:	85 to 2560 mg/m^3 (20 to 600 ppm)
OSHA PEL:	850 mg/m^3 (200 ppm) - Ceiling
	425 mg/m^3 (100 ppm) - TWA
Recommended Flow Rate:	0.2 L/min
Breakthrough Time:	111 min @ 0.2 L/min and 1710 mg/m^3

Suppose it is desired to determine both ceiling and TWA exposures of workers exposed to styrene and the concentrations are unknown.

Ceiling Determination: If sampling were done at 0.2 L/min for 30 min and a total sample volume of 6 L collected which is above the 5 L recommended sample volume, would this a problem? Probably not. For instance, in the breakthrough test, a concentration of 2 times the OSHA Ceiling Standard (1710 mg/m^3) was sampled at 0.2 L/min for 111 min (22.2 L) before breakthrough occurred, collecting a total weight of 38 mg of styrene. Of course, this test was conducted in a dry environment with only styrene present. A safety factor of 50% should be allowed to account for humidity effects. Thus, if sampling is done for about 55 min at 0.2 L/min, levels of styrene up to 400 ppm could still be collected without sample breakthrough.

Also to be considered are the other organics present. If a concentration of 200 ppm acetone exists in this environment, then an additional safety factor should be added. An arbitrary 50% reduction in total sampling time or 28 min at 0.2 L/min might be done. This is very close to the original sampling time of 30 min. With the safety factors built in, collecting a 6-L sample should not be a problem. Alternately, the flow could be reduced to 0.1 L/min and be well within the 5-L total volume.

TWA Determination: In this same situation, the goal is to collect 8-hr samples for comparison to the 100 ppm TWA. If sampling was done at 0.05 L/min, then the total sample volume would be 22.5 L, substantially above the 5-L recommended sample volume. If the flow was dropped to 0.02 L/min, then the sample volume would be 9 L. This sample volume might be acceptable if the styrene concentrations are around 100 ppm and no other competing organics are present, e.g., acetone. However, the safer approach would be to collect two consecutive samples at 0.02 L/min for 4 hrs (total sample volume of 4.8 L each).

2. Pushing a Method to the Limit, Limit of Quantitation

Given Parameters:	Method 2502 for Formaldehyde
Recommended Sample Volume:	12 L @ 0.05 L/min
Working Range:	0.3 to 5 mg/m^3 (0.25 to 4 ppm)
Limit of Detection:	1 to 4 µg HCHO per tube, depending on media blank value

In this particular example, the object is to estimate exposure to formaldehyde down to 0.1 ppm (0.12 mg/m^3) which is below the lowest tested concentration of formaldehyde (0.55 mg/m^3). In order to collect 4 µg of formaldehyde (the limit of quantitation) at this concentration, 33 L of air (0.12 mg/m^3 or 0.12 µg/L x 33 L = 4 µg) would have to be collected. This volume is substantially above the recommended sample volume of 12 L. Since the recommended sample volume is generally a conservative value used to protect against breakthrough under worse case conditions, i.e., high humidity and high concentrations, considerable leeway exists for exceeding this value. In pushing a method to the limit, it is often necessary to sample beyond the breakthrough volume, while observing recommended maximum sampling flow rate, in order to obtain the sensitivity to determine the concentration of interest. If this is done, then the risk must be accepted that the method may not work outside the limits tested. In this method, the additional factor of a measurable (although possibly variable between sampler lots) media blank value represents a major limiting factor on the lower end of the working range. For instance, the presence of high relative humidity and other organic solvents will severely reduce the number of active sites available on the sorbent for collection of the contaminant of interest. The best approach is to consult with the analytical laboratory and then to take a sufficient number of samples to determine the useful limits of the sampler in the particular application.

3. BULK SAMPLES

The addition of bulk samples can often make the difference between a successful or unsuccessful sampling effort. This is especially true where there is mixed solvent exposure or unknown dust exposure and for determining silica content of dusts. The primary purpose of bulk samples is to provide the analytical laboratory with a large enough sample for qualitative and sometimes quantitative analysis. The two major types of bulk samples are bulk air and mass bulk (liquid or solid) samples.

a. Bulk Air Samples

Generally, a bulk air sample is defined as a large volume area sample collected for the purpose of qualitative analysis. A good example is multiple solvent exposure where the exact identity of the airborne solvents is unknown, e.g., painting operations. For most organic solvents, a bulk air consists of a charcoal tube (or whatever sorbent is called for) collected at 1 L/min for several hours. Although the sample is likely to exhibit breakthrough, this does not matter since one is primarily interested in what substances are present rather than their exact concentrations (the latter aim is accomplished through the separate collection of proper samples). Any questions concerning how or whether or not a bulk air sample is needed should be addressed to the analytical laboratory prior to sampling. In the case of silica, either a bulk air or solid bulk (e.g., a rafter sample) or both are suggested so that enough material will be available to determine free silica content.

b. Bulk Liquids and Solids

Collection of bulk materials may be needed to establish the substances present in the workplace and, in some cases, to establish the relative levels of certain substances present in the raw material. A good example of the latter is the case of mixed solvent exposure when determining if a certain contaminant of interest is present, e.g., benzene. In some cases, a list of 30 solvents may be present (from Material Safety Data Sheets), but it is not certain which ones are present or in what proportions. This example is also true for dusts, as was discussed previously for silica, or for metals which may exist in trace quantities.

In choosing bulk samples, the end goal must be considered: qualitative and/or quantitative analysis. In the case of a painting operation, it is preferred to have the bulk samples separated by contaminants of interest, i.e., solvent fraction separate from the pigment fraction. This allows the laboratory to analyze the different portions of the paints without having to go through a lengthy separation process. In general, the cleaner the bulk, the easier it will be for the laboratory to conduct the analysis. In many cases, the industrial hygienist is interested in a "dirty" bulk. Any information that can be given to the laboratory on what may or may not be present will help speed up the analysis. Advance consultation with the laboratory is desirable.

In choosing bulk dust samples, the sample should be representative of the airborne dust to which the workers are being exposed. Usually this is a settled dust sample collected from rafters or near the workers' jobsite. In other cases, a process dust sample is chosen to determine the composition of the material before it is airborne. In cases where the choice is not clear, do not follow the adage that "more is better." Bulk samples should be limited in number to optimize the laboratory's time. A good approach, when in doubt as to what bulks are needed, is to collect several but to allow the laboratory to analyze only those needed to answer questions as they arise.

When shipping bulks, care must be taken to preserve the integrity of the samples and to follow established Department of Transporation (DOT) shipping regulations. Only 5 to 10 mL of the liquid or solid is needed, so keep bulk sample sizes small. In general, leak-proof glass containers are best since they will not react with most chemicals; however, polyethylene containers can be used in the majority of cases. A convenient container is a 20-mL scintillation vial with PTFE-lined cap. Specific chemicals for which polyethylene containers should not be used include aromatic compounds, chlorinated hydrocarbons and strong acids. The lids of the containers should be sealed with shrink bands or tape for further assurance against leakage. These containers should be labeled as required by DOT under their regulations, 49CFR Part 171-177. For most materials classified as "Flammable" or "Poisonous," amounts up to 1 quart can be shipped by any carrier. Most bulk dusts are not covered by DOT regulations. Specific restrictions and labelling requirements should be checked prior to shipping any samples.

In the case of volatile bulk samples (and some air samples), consideration should be given to shipping the samples on dry ice or with bagged refrigerant (e.g., "blue ice"). Again, check with the carrier you plan to use as there may be restrictions on the amount of dry ice they will accept in a package (usually 5 pounds or less is acceptable). Specific labels are usually required when dry ice is used.

4. BLANKS

Certain numbers of blanks are required by the analytical laboratory for each set of samples to be analyzed. The specific method being used should be consulted concerning the number and type of blanks required. There are two types of sampler blanks: field and media blanks. Field blanks are clean samplers taken to the sampling site, handled in every way as the air samples, except that no air is drawn through them. Media blanks are simply unopened, new samplers which are sent with the samples (these blanks are not usually taken to the field). It is also recommended that additional blind field blanks be sent along with the field samples, labelled as field samples, as a further check on the analysis. Blanks are good insurance to deal with contamination, but the best approach is to avoid sample contamination by being careful. The recommended practice for the number of field blanks is two field blanks for each 10 samples with a maximum of 10 field blanks for each sample set. Approximately five media blanks should also be included. Again, consult the specific method for the number and type of blanks as these numbers will vary.

Another frequently-used practice is to include blind spiked samples as a quality control check of the analytical laboratory (see pages 9 and 10). See page 31 for a detailed discussion of spiking procedures.

5. DIRECT-READING METHODS

The variety of types and costs of direct-reading methods available is large and expanding, including detector tubes (both short- and long-term), aerosol monitors, integrating passive monitors for certain gases and portable instrumentation for gas chromatography or infrared spectroscopy [4]. Many direct-reading instruments now used for personal or area measurements have evolved from laboratory or process control instruments [5].

Some of the considerations (i.e., specificity and sensitivity) for the use of direct-reading methods for quantitative determinations are similar to those already given for classical filter or sorbent methods. In many cases, direct-reading instruments, which are physically small and portable, qualify as personal sampling devices.* These offer the additional advantages over classical methods by reducing labor and analytical costs and may be the methods of choice when instantaneous results are important, even at the expense of some degree of sensitivity or specificity. In general, manufacturers' instructions should be followed in the calibration and use of these devices. Due to the severe conditions to which direct-reading instrument may be subjected, performance checks and preventive maintenance on a periodic basis or before each use are very important. Many direct-reading instruments are powered by Ni-Cd batteries which can fail to provide a full charge over the full sampling period unless frequently or fully discharged and recharged several times just prior to use. An additional responsibility, that of field calibration of the direct-reading instrument, falls on the field sampling personnel.

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*A portable instrument is defined as weighing less than 4.5 kg (10 lbs.) and powered by self-contained batteries [6]. For personal monitoring, the instrument configuration should be such that the breathing zone can be monitored. Alarms, both audible and visual, and hard-copy documentation are desirable.

6. SAMPLING STRATEGY

To obtain the maximum amount of information during the course of a survey with a minimum amount of samples, a statistical sampling strategy should be developed before conducting any survey [7,8]. Several pieces of information must be known in advance to plan a sampling strategy, including the size of the workforce to be sampled, the accuracy of the sampling and measurement method to be used and the confidence one wishes to have in predicting the exposure of the workforce. For example, to determine with 90% confidence that at least one worker from a workplace subgroup will be in the top 10% of the exposures occurring in the group, the number of employees to sample would be chosen from Table 3. Other tables are given in the publication for confidence limits of 95% and for the top 20% of exposures. Again, judicious use of sampling statistics will optimize the number of samples needed.

Table 3. Minimum sample size (n) for including (@ 90% confidence level) at least one high risk employee* [7].

Size of Employee Group (N):																		
1	2	3	4	5	6	7	8	9	10	11-12	13-14	15-17	18-20	21-24	25-29	30-37	39-49	50	∞
Minimum Number of Measured Employees (n):																			
1	2	3	4	5	6	7	7	8	9	10	11	12	13	14	15	16	17	18	22

*Exposure in highest 10% of N.

7. SAMPLING TECHNIQUE

The following are suggested general techniques for active sampling using some of the more common samplers. Consult individual methods for details of sample size. Also, where appropriate, instructions for passive (diffusive) sampling and the use of direct-reading instruments appear in individual methods.

a. Calibration of Personal Sampling Pumps

The accuracy of determination of the concentration of a toxic substance in air is no greater than the accuracy with which the air volume is measured. Therefore, accurate calibration of the airflow rate through the sampling train is necessary. The frequency of calibration depends on the use, care and handling to which the pump is subjected. In addition, pumps must be recalibrated if they have been abused and after each repair. Ordinarily, pumps should be calibrated in the laboratory and the field, both before field use and after each field survey.

The choice of a reference instrument will depend on where the calibration is to be performed. For laboratory use, primary standards, such as a spirometer or soap-bubble meter, are recommended. Other instruments, such as a wet-test or a dry-gas meter, may be used. The following instructions are for the soap-bubble meter. If another instrument is used, equivalent procedures should be followed.

(1) Set up the apparatus as shown in Figure 1.

(2) Check the pump battery with a voltmeter to assure adequate voltage. Charge the battery if necessary.

(3) Turn the pump on and moisten the inner surface of the soap-bubble meter with the soap solution. Draw bubbles upward until they travel the entire length of the buret without breaking.

(4) Adjust the pump to the desired nominal flow rate. Check the water manometer. The pressure drop across the sampler should not exceed 2.5 cm Hg (13 inches) of water.

(5) Start a soap bubble in the buret and measure the time, with a stopwatch, that it takes to traverse two calibration marks. For a 1000-mL buret, a convenient calibration volume is 500 mL. Repeat the determination at least twice more. Average the results and calculate the flow rate by dividing the calibration volume by the average time.

(6) Record the following data:
   a. volume measured;
   b. elapsed time;
   c. pressure drop;
   d. air temperature;
   e. atmospheric pressure;
   f. serial number of the pump;
   g. pump model; and
   h. date and name of operator.

(7) If the sampling pump used for sample collection uses a variable area flow meter (rotameter) for flow rate indication, the calibrated flow rate must be adjusted for the actual air pressure and temperature during sampling. The expression for this correction is:

$$V \text{ (Corrected volume, L)} = Q \cdot t \, (P_C T_S / P_S T_C)^{0.5}$$

where: Q = indicated flow rate (L/min)
t = sampling time (min)
P_C = pressure during calibration of sampling pump (kPa or other pressure units)
P_S = pressure of air sampled (same units as P_C)
T_C = temperature during calibration of sampling pump (K)
T_S = temperature of air sampled (K).

This correction is <u>not</u> used for non-rotameter sampling pumps.

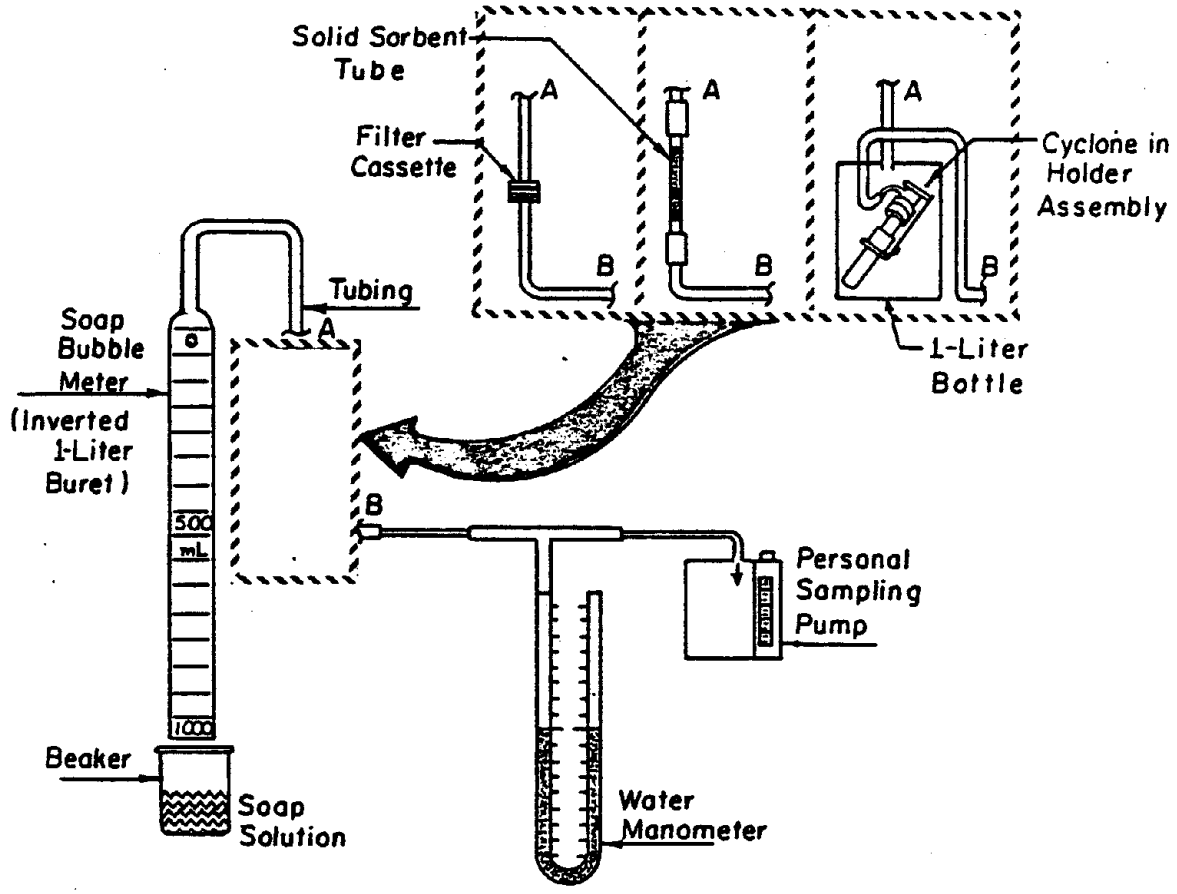

Figure 1. Calibration Apparatus.

b. Sampling Instructions for Solid Sorbent Tube Sampler

Use these instructions for active personal sampling (i.e., pumped sample airflow) for substances which are retained on solid sorbents such as activated charcoal, silica gel, porous polymers, etc.

(1) Calibrate each personal sampling pump at the desired flow rate with a representative solid sorbent tube in line,* using a bubble meter or equivalent flow measuring device. (*Alternatively, use a flow restrictor to provide a pressure drop equal to that of the average solid sorbent tube.)

(2) Break the ends of the solid sorbent tube immediately before sampling to provide an opening at least one-half of the internal diameter at each end.

(3) Connect the solid sorbent tube to a calibrated personal sampling pump with flexible tubing with the smaller sorbent section (backup section) nearer to the pump. Do not pass the air being sampled through any hose or tubing before entering the solid sorbent tube. Position the solid sorbent tube vertically during sampling to avoid channeling and premature breakthrough.

(4) Prepare the field blanks at about the same time as sampling is begun. These field blanks should consist of unused solid sorbent tubes from the same lot used for sample collection. Handle and ship the field blanks exactly as the samples (e.g., break the ends and seal with plastic caps) but do not draw air through the field blanks. Two field blanks are required for each 10 samples with a maximum of 10 field blanks per sample set.

(5) Take the sample at an accurately known flow rate as specified in the method for the substance and for the specified air volume. Typical flow rates are in the range 0.01 to 0.2 L/min. Check the pump during sampling to determine that the flow rate has not changed. If sampling problems preclude the accurate measurement of air volume, discard the sample. Take two to four replicate samples for quality control for each set of field samples.

(6) Record pertinent sampling data including location of sample, times of beginning and end of sampling, initial and final air temperatures, relative humidity and atmospheric pressure or elevation above sea level.

(7) Seal the ends of the tube immediately after sampling with plastic caps. Label each sample and blank clearly with waterproof identification.

(8) Pack the tubes tightly with adequate padding to minimize breakage for shipment to the laboratory. In addition to the sample tubes and field blanks, ship at least six unopened tubes to be used as media blanks so that desorption efficiency studies can be performed on the same lot of sorbent used for sampling.

(9) Ship bulk samples in a separate package from the air samples to avoid contamination of the samples. Suitable containers for bulk samples are glass with a polytetrafluoroethylene (PTFE)-lined cap, e.g., 20-mL glass scintillation vials.

c. Sampling Instructions for Filter Sampler

Use these instructions for personal sampling of total (respirable and non-respirable) aerosols. Methods requiring these instructions specify FILTER as the sampling method. These instructions are not intended for respirable aerosol sampling.

(1) Calibrate the personal sampling pump with a representative filter in line using a bubble meter or equivalent flow measuring device.

(2) Assemble the filter in the two-piece cassette filter holder. Support the filter by a stainless steel screen or cellulose backup pad. Close firmly to prevent sample leakage around the filter. Seal the filter holder with plastic tape or a shrinkable cellulose band. Connect the filter holder to the personal sampling pump with a piece of flexible tubing.

(3) Remove the filter holder plugs and attach the filter holder to the personal sampling pump tubing. Clip the filter holder to the worker's lapel. Air being sampled should not be passed through any hose or tubing before entering the filter holder.

(4) Prepare the field blanks at about the same time as sampling is begun. These field blanks should consist of unused filters and filter holders from the same lot used for sample collection. Handle and ship the field blanks exactly as the samples, but do not draw air through the field blanks. Two field blanks are required for each 10 samples with a maximum of 10 field blanks per sample set.

(5) Sample at a flow rate of 1 to 3 L/min until the recommended sample volume is reached. Set the flow rate as accurately as possible (e.g., within $\pm$ 5%) using the personal sampling pump manufacturer's directions. Take two to four replicate samples for quality control for each set of field samples.

(6) Observe the sampler frequently and terminate sampling at the first evidence of excessive filter loading or change in personal sampling pump flow rate. (It is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air.)

(7) Disconnect the filter after sampling. Cap the inlet and outlet of the filter holder with plugs. Label the sample. Record pertinent sampling data including times of beginning and end of sampling, initial and final air temperatures, relative humidity and atmospheric pressure or elevation above sea level. Record the type of personal sampling pump used and location of sampler.

(8) Ship the samples to the laboratory as soon as possible in a suitable container designed to prevent damage in transit. Ship bulk material to the laboratory in a glass container with a PTFE-lined cap. Never store, transport or mail the bulk sample in the same container as the samples or field blanks. In addition to the samples and field blanks, ship five unopened samplers from the same lot for use as media blanks.

d. Sampling Instructions for Filter + Cyclone Sampler

Use these instructions for personal sampling of respirable aerosols (ACGIH definition [9]). Methods requiring these instructions specify CYCLONE + FILTER as the sampling method.

(1) Calibrate the pump to 1.7 L/min, with a representative cyclone sampler in line using a bubble meter or a secondary flow measuring device which has been calibrated against a bubble meter. The calibration of the personal sampling pump should be done close to the same altitude where the sample will be taken.

(2) Assemble the pre-weighed filter in the two-piece cassette filter holder. Support the filter with a stainless steel screen or cellulose backup pad. Close firmly to prevent sample leakage around the filter. Seal the filter holder with plastic tape or a shrinkable cellulose band.

(3) Remove the cyclone's grit cap and vortex finder before use and inspect the cyclone interior. If the inside is visibly scored, discard this cyclone since the dust separation characteristics of the cyclone might be altered. Clean the interior of the cyclone to prevent reentrainment of large particles.

(4) Assemble the two-piece filter holder, coupler, cyclone and sampling head. The sampling head rigidly holds together the cyclone and filter holder. Check and adjust the alignment of the filter holder and cyclone in the sampling head to prevent leakage. Connect the outlet of the sampling head to the personal sampling pump by a 1-m piece of 6-mm ID flexible tubing.

(5) Clip the cyclone assembly to the worker's lapel and the personal sampling pump to the belt. Ensure that the cyclone hangs vertically. Explain to the worker why the cyclone must not be inverted.

(6) Prepare the field blanks at about the same time as sampling is begun. These field blanks should consist of unused filters and filter holders from the same lot used for sample collection. Handle and ship the field blanks exactly as the samples, but do not draw air through the field blanks. Two field blanks are required for each 10 samples with a maximum of 10 field blanks per sample set.

(7) Turn on the pump and begin sample collection. If necessary, reset the flow rate to the pre-calibrated 1.7 L/min level, using the manufacturer's adjustment procedures. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, observe the filter and personal sampling pump frequently to keep the flow rate within $\pm$ 5% of 1.7 L/min. The sampling should be terminated at the first evidence of a problem.

(8) Disconnect the filter after sampling. Cap the inlet and outlet of the filter holder with plugs. Label the sample. Record pertinent sampling data including times of beginning and end of sampling, initial and final air temperatures and atmospheric pressure or elevation above sea level. Record the type of personal sampling pump, filter, cyclone used and the location of the sampler.

(9) Ship the samples and field blanks to the laboratory in a suitable container designed to prevent damage in transit. Ship bulk samples in a separate package.

(10) Take two to four replicate samples for every set of field samples to assure quality of the sampling procedures. The set of replicate samples should be exposed to the same dust environment, either in a laboratory dust chamber or in the field. The quality control samples must be taken with the same equipment, procedures and personnel used in the routine field samples. The relative standard deviation, s_r, calculated from these replicates should be recorded on control charts and action taken when the precision is out of control.

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E. DEVELOPMENT AND EVALUATION OF METHODS

by R. DeLon Hull, NIOSH/DPSE

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1. METHODS DEVELOPMENT AND EVALUATION STRATEGIES

The development and evaluation of analytical methods that are useful, reliable and accurate for most industrial hygiene monitoring problems requires the application of some general guidelines and evaluation criteria. This is particularly important when methods are developed by different individuals and organizations (e.g., contractors) and compiled into a single manual. Adherence to guidelines should minimize overlooking potential problems in the methodology during its development, as well as provide cohesiveness and uniformity to the manual that is compiled. Likewise, a generalized set of evaluation criteria should be applied for the evaluation of sampling and analytical methodology.

The methods in this Manual were developed and evaluated using an established experimental protocol for that specific analyte. Generally, the protocol developed for the joint NIOSH/OSHA Standards Completion Program (SCP) [1,2] was used as the basic framework for the methods development protocols. A somewhat broader strategy which incorporates the salient features of the SCP protocol [1,2,3] as well as other protocols used in NIOSH and other methods development work [4,5,6,7,8] will be discussed in this chapter.

The recommended strategy is presented in the following sections. This strategy incorporates both laboratory and field experimentation in developing and evaluating methods. Laboratory generation of test atmospheres of analyte is a necessary and important part of this development and evaluation process. The strategy is relevant for active, as well as passive, sampling systems.

2. DEVELOPING PRELIMINARY INFORMATION

a. Definition of Analyte

Development of analytical methodologies by NIOSH is typically initiated by requests from NIOSH field personnel or other agencies [e.g., Occupational Safety and Health Administration (OSHA), Mine Safety and Health Administration (MSHA), Bureau of Mines (BOM), etc.]. In developing these methodologies, it is important to be sure the method is specific for the analyte (e.g., the OSHA NaOH standard calls for a method which will determine sodium hydroxide in the presence of sodium salts and other cations).

b. Literature Search

In addition to reviewing the literature for analytical methodologies developed by others, the search should also include defining physical properties, chemical reactions, toxic properties of the analyte as well as analytical reagents used in its determination, and industrial operations and interferences where exposure may occur. OSHA permissible exposure limits [9], NIOSH recommended standards [10], ACGIH threshold limit values [11], EPA standards and other appropriate sources should be used to establish a target concentration at which the methods development and evaluation work will be conducted.

c. Proposed Method

Findings from the literature search are used to develop proposed analytical methodology. In developing this methodology, the sensitivity of the analytical technique in relation to the target concentration of the analyte in air must be considered, as well as the sample collection scheme. Collection of samples for laboratory analysis is typically accomplished by filtration, adsorption, absorption or chemical reaction; however, in some cases, "whole air" or "bag" samples are used. Also, it is impractical to develop samplers that are too cumbersome to be worn by workers, that contain chemicals that are too hazardous to be worn by workers, or that require constant attention by the industrial hygienist conducting the sampling. Because of these reasons, bubbler, bag and impinger methods are considerably less desirable than filters, solid sorbents, passive monitors or personal direct-reading instrumentation.

3. LABORATORY TESTING

a. Evaluation of Measurement Parameters

(1) Measurement Range. The useful range of the measurement system must be determined following optimization of the sensitivity and selectivity of the measurement system. This typically includes an estimate of the limit of detection (LOD) and the measurement range. The limit of quantitation (LOQ) is typically defined as the point at which the relative standard deviation of the measurement approximates 10% with the upper end typically defined by the deviation of the calibration curve from linearity. For OSHA compliance sampling, the analytical range should be sufficient to allow analysis of samples ranging from at least one-half to two times the standard for which the method is being developed (for a nominal sampling volume) without excessive dilution.

(2) Measurement Precision. The measurement precision is determined by pooling the standard deviations found for several points over the measurement range, providing that homogeneity of variance exists [1,2]. Four determinations at five different concentrations gives 15 degrees of freedom for the precision estimate. The pooled precision should be sufficiently low (better than 7 or 8% relative standard deviation) so that when combined with the imprecision of sampling (e.g., pump error), the total precision is still acceptable [1,2].

(3) Measurement Interferences. Potential interferences in the measurement methodology should be investigated and defined. The literature search should be used to help identify substances in workplace environments which would likely be collected with the analyte and could cause erroneous analytical measurements. The measurement conditions should be adjusted to eliminate or minimize these interferences. Interferences which cannot be eliminated should be defined.

b. Evaluation of Sampling Parameters

(1) Recovery From Collection Media. Before investigating the factors affecting analyte collection, it is necessary to verify that the analytical methodology used is accurately determining the quantity of material collected. A means for accomplishing this is fortification (spiking) of the sorbent material (solid sorbent, filter or solution) with a suitable solvent containing dissolved quantities of analyte representative of exposures at 0.1, 0.5, 1 and 2 times the target concentration (Section 2.b.); equilibration of analyte and sorbent; followed by desorption or digestion; and analysis. Spiking is normally accomplished by pipetting an analyte containing solvent (preferably less than 10 µL) directly onto the sorbent. This method of spiking has been shown to be comparable to dynamic sampling for a number of organic compounds on charcoal [12]. Direct gas spiking has also been done by injecting gaseous analytes into a gas stream passing through the sampler. In calculating the quantity of analyte necessary for spiking, a sampling time of 8 hours should be used for time-weighted average measurements and 15 minutes for ceiling measurements, unless previous experimentation has shown that shorter sampling times are necessary. For the 0.5, 1 and 2 times the target concentration, recoveries of greater than or equal to 90% are preferred although recoveries greater than or equal to 75% may be acceptable [1,2,3,4]. Recoveries greater than or equal to 75% at the 0.1 times the target level are required if validation of the methodology at that level is necessary.

(2) Capacity of Collection Media. Capacity of samplers is usually reported in terms of breakthrough volumes or collection efficiency. Breakthrough volume is determined for solid sorbent tubes, bubblers and impingers by sampling a test atmosphere at 2 times the target value and greater than 80% relative humidity until the sampler effluent reaches an analyte concentration of 5% of the tube influent concentration [3]. The sampler effluent is most easily monitored using direct-reading instrumentation but may also be accomplished with several sampling tubes used consecutively for short sampling times. The efficiency of particulate collection by filtration is also determined using alternate backup

sampling devices or similar samplers in series. For passive samplers, capacity is determined by sampling for times varying from 7.5 minutes to 12 hours. Sampler capacity is exceeded when the analyte uptake rate is no longer constant or predictable. Because of potential competition for sorbent sites with other substances that may be present in workplace atmospheres, a safety factor of 0.67 is multiplied with the laboratory-determined capacity and the product is reported as the useful capacity of that sampler. Filters also have a limited capacity which generally is manifested in the increased pressure drop at high loadings. Oils and mists, as well as high loadings of other aerosols, will increase pressure drop across the filter. A maximum loading of 2 mg total dust is recommended to avoid losses due to mechanical sloughing of the collected aerosol from the filter.

(3) Stability of Collected Analyte. The stability of collected analyte on samplers (storage after sampling) must be determined for all samplers that are returned to laboratories for analysis. Sample storage stability is usually investigated by exposing several samplers to 1 times the PEL concentrations of analyte and 80% relative humidity. One set of samples (6 to 10 samples per set) is analyzed immediately following exposure, a second set after 1 week room temperature storage and a third set after 2 weeks refrigerated storage [3,4]. Sampling systems are termed stable if the difference in the means for the immediately analyzed and the stored samples is less than 10%.

(4) Sampling Interferences. Various potential sampling interferences will certainly be encountered under actual use and, consequently, should be investigated during method development. Moisture (humidity) is a potential coadsorbent, the concentration of which may change daily and will certainly be different for different industrial processes and facilities. Moisture and other substances present may also affect the stability of collected gases and aerosols (e.g., hexavalent chromium; see Method 7600). Other species which are likely to be present in workplace environments and are potential sampling interferences (e.g., competing for sorbent sites) should also be investigated. The extent of interference for these species should be defined.

(5) Overall Precision. The overall precision of sampling and measurement is determined by collecting several samples over the working range of the method. Typically, 6 to 10 samples at each of 3 (0.5, 1 and 2 times the target value) or 4 (0.1, 0.5, 1 and 2 times the target value) concentration levels are used to determine a pooled relative standard deviation providing homogeneity of variance exists [1,2,3,4]. The pooled relative standard deviation for unbiased methods must be less than 0.105 for the total analytical error to be less than 25% in at least 95% of the samples analyzed [1,2].

(6) Overall Bias. The overall bias of sampling and measurement is generally determined from the same samples collected for the overall precision study. The mean concentration determined by the samples must be within 10% of the concentration determined by an independent method. In reporting biases found, the independent method used must be well defined including its known characteristics and limitations (accuracy, precision,

interferences, etc.). In addition, any uncorrected analytical bias, in conjunction with the sampling and measurement precision, must meet the ± 25% criterion previously discussed [1,2].

c. Evaluation of Parameters Specific to Sampler Types

(1) Pressure Drop Across Active Samplers. The pressure drop across active (pumped) samplers must be determined at the flow rate at which these devices will be used. The pressure drop must be sufficiently low that sampling pumps will function properly for the desired sampling period. See page 17 for characteristics of currently available sampling pumps. As noted in b.(2) on the previous page, the pressure drop across membrane filters is a function of total aerosol collected.

(2) Sorbent Stability. Sorbents coated with reactive substrate are finding increased usage because of their specificity for certain analytes. Bubbler and impinger chemistries are also being applied to these solid sampling devices which are more acceptable to workers. The shelf life of these samplers must be determined since the reagents or derivatizing agents may evaporate from the substrate, atmospheric moisture may be absorbed by the sampling medium or reagent coatings may react with atmospheric gases (CO_2, etc.). The occurrence of any of these possibilities is likely to affect adversely the capacity of the sampler.

(3) Passive Samplers. Passive or diffusional samplers must also be investigated for the effects of reverse diffusion, sampler starvation, monitor orientation and temperature effects [4]. Reverse diffusion is checked by exposing two sets of samplers to analyte for some period of time (approximately one-half of a typical work shift, e.g., 4 hours), analyzing one set of samplers after this exposure and exposing the other set of samplers to an analyte-free environment for the same amount of time as the initial exposure. Sampler starvation is typically checked at low (ca. 25 ft/min.) and high (ca. 250 ft/min) face velocities. The effect of sampler orientation on sample collection is determined by exposing samplers to analyte with several samplers positioned parallel and others perpendicular to the direction of airflow. The effect of ambient temperature on sample collection must be determined since diffusion constants are temperature dependent and permeation membranes used in some diffusional samplers are temperature-dependent. Temperature effects are found by determining recoveries after exposures in low (ca. 10 °C) and high (ca. 40 °C) temperature environments.

(4) Direct-Reading Field Instrumentation. Several of the factors previously discussed are applicable to direct-reading instrumentation (e.g., range, precision, interferences and bias) while others do not directly apply (e.g., capacity and recovery from collection media). Stability of the instrumentation system, more correctly termed reproducibility, includes zero and span drift, background noise and calibration stability. Other factors requiring investigation include instrument warm-up time, frequency of need and ease of field calibration, response time, response linearity, run time with batteries, and specificity. The influence of ambient conditions (temperature and pressure) must be known [13]. During field testing, the effects of spurious radiation (e.g., RF radiation from sealers) should also be investigated.

4. FIELD TESTING

a. Precision

Precision of sampling and measurement in an actual workplace environment is most readily determined by collecting at least 10 replicate samples from a homogeneous atmosphere. This can be accomplished using a field exposure chamber [5]. Overall precision can also be determined by collecting several sets of samples (at least two samples per set). In this instance, the sample sets do not have to be collected from a homogeneous atmosphere; however, a considerably larger number of samples must be collected. Field precision should be compared with laboratory-determined precision. A large increase in field-determined precision over laboratory-determined precision is indicative of uncorrected interfering species present in the workplace environment, the use of a sampling and measurement system that is not rugged, or sampling from an inhomogeneous atmosphere.

b. Bias

Sampling and measurement bias should also be determined in workplace environments [5]. This is also accomplished most easily with a field exposure chamber and requires the use of independent methods for estimating the analyte concentration.

c. Personal Sampler Durability

Sampler durability is a subjective determination which is estimated by conducting personnel sampling. Sample losses due to breakage or leakage of the sampler, worker discomfort because of the sampler, the amount of time required by the industrial hygienist for sampler set-up, monitoring and take-down all should be minimal.

5. USER CHECK AND DOCUMENTATION

As a check on the clarity of new methods, they should be reviewed and submitted to a user check (i.e., the method is used to analyze spiked or generated samples of known concentration by someone other than the researcher who developed it) and to a collaborative test, if feasible. Also, a backup report should be written detailing the experimentation used in the methods development work.

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F. SPECIAL CONSIDERATIONS FOR BIOLOGICAL SAMPLES

by Larry K. Lowry, Ph.D., NIOSH/DBBS

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1. GENERAL CONSIDERATIONS

Biological monitoring is a rapidly emerging science that is finding increased use, both in the United States and abroad. It is often used in conjunction with environmental monitoring to describe more completely exposures and absorption of chemicals found in the workplace. Specifically, biological monitoring includes the measurement of the absorption of an environmental chemical in the worker. In order to accomplish this measurement, biological specimens are analyzed for the chemical agent, its metabolite or some specific effect on the worker. Some examples include the measurement of blood lead as an assessment of chronic lead exposure, measurement of urinary phenol for assessment of exposure to benzene, and measurement of carboxyhemoglobin in blood as an index of carbon monoxide or methylene chloride exposure. In a broader sense, biological monitoring may include behavioral and performance testing and medical procedures.

Biological monitoring, unlike environmental monitoring, should be considered a medical procedure since, by definition, the specimen comes directly from a human. Therefore, such areas as informed consent, medical-legal ethics and the Federal Privacy Act need to be considered.

Biological monitoring has been called the ultimate personal sampler because, when properly used, it can assess worker exposure to industrial chemicals by all routes including skin absorption and ingestion. An area often overlooked, however, is the measurement of actual uptake of environmental agents, and the suitability of biological monitoring to assess inhalation uptake, which is:

(respiratory volume)•(environmental concentration)•(length of exposure).

Another use of biological monitoring is to assess the effectiveness of engineering controls or work practices to limit uptake of environmental chemicals.

Biological monitoring is not without its limitations. A major limitation is the lack of detailed information on the fate of industrial chemicals in humans. Most of the toxicological/pharmacological information available is from experimental animals and not easily applied to humans. Another concern is the apparent wide variability seen in the majority of biological monitoring data. Proper knowledge

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of the fate of a chemical, its pharmacokinetic properties, specific methodologies and other factors described later can control such variability; however, specific methodology and data interpretation remain an obstacle to widespread use of biological monitoring. Research is underway worldwide to develop more definitive methods and to better define dose-response relationships and suggested limit values.

2. SPECIFIC FACTORS TO BE CONSIDERED WHEN CONTEMPLATING BIOLOGICAL MONITORING

Considerable advance planning is necessary when biological monitoring is contemplated to aid in the selection of the appropriate test and to ensure data that will be meaningful in assessing worker exposure. These factors fall into two areas: (1) the characteristics of the exposure, and (2) the characteristics of the chemical in workers. The type of exposure (i.e., chronic, acute, intermittent), the major route of exposure (i.e., dermal, inhalation, ingestion) and the nature of other workplace chemicals are important considerations when contemplating biological monitoring. For example, one should not select the FEP (free erythrocyte protoporphyrin) or ZPP (zinc protoporphyrin) tests to assess a recent acute exposure to lead but should select the δ-aminolevulinic acid dehydratase (ALAD) test which responds rapidly to lead exposure.

The fate of a chemical in humans is also important. It is necessary to know how the body metabolizes (biotransforms) the chemical, where the analyte of interest is present in measurable quantities (i.e., what sample should be collected) and some knowledge of the pharmacokinetics of the chemical in humans (i.e., when should the specimen be collected). If all of these factors are considered, then a successful biological monitoring program is possible.

3. PRACTICAL CONSIDERATIONS

a. Selection of Methods. A dialog between the occupational health professional familiar with the workplace and a competent laboratory chemist is a requirement for proper method selection. The following areas should be addressed:

(1) Does the survey require rapid, semi-quantitative (non-specific) or specific methodologies?

(2) Do interferences exist from diet, drugs, alcohol, disease states or other workplace chemicals? If so, can these interferences be controlled?

(3) Does the sample matrix affect the analysis? In general, blood serum and urine specimens require different sample preparation and may require separate methodologies to eliminate matrix effects.

(4) Is the limit of detection low enough to differentiate exposed from non-exposed workers? The method may have been developed when exposure limits were higher.

(5) Does the method have guidelines for interpretation of the data or are published guidelines/normals available? If not, can non-exposed workers be used for controls or reference baseline data?

b. Sampling Strategy. Strict attention to sample integrity is essential for quality data. The ideal "perfect" laboratory method and trained analyst cannot produce good results unless:

(1) the correct specimen is collected;

(2) the specimen is collected at the right time after exposure to the toxic substance;

(3) the proper container, with preservative or anticoagulant, is used;

(4) the proper field specimen preparation is used;

(5) the specimen is not contaminated;

(6) the stability of the analyte is assured through proper shipment of the specimen to the laboratory; and

(7) the specimen is properly labeled.

The details of biological sampling are shown in the individual methods. They are important.

c. Quality Assurance. Good data require the utilization of an effective quality control program. Two major areas need attention: (1) laboratory quality control and (2) field quality control.

There are different approaches used in laboratory quality control programs in biological monitoring since few proficiency testing programs are available. Acceptable precision can be maintained for a method by the preparation of a pooled specimen in a biological matrix, aliquoting the pooled specimen into multiple containers, properly preserving the pooled specimens (usually in a freezer) and running a pooled sample with each batch of samples. Quality control charts should be prepared after a minimum of 20 analyses of "pool" and acceptable control guidelines are prepared. When a batch of analyses containing a "pool" value is out of control, results from that entire batch should not be reported until the source of error is corrected.

Accuracy is difficult to substantiate in the absence of proficiency testing programs. Strict attention to such items as standardization, extraction efficiency, recovery, standard stability, reagent and specimen stability, as well as proper instrument calibration, are mandatory. Many gas and liquid chromatographic methods utilize internal standards and results are reported using response factors aiding in instrument quality assurance.

Quality control at the field level can be maintained and the laboratory checked by:

(1) ensuring sample integrity, i.e., proper collection, preservation and shipment procedures;

(2) submitting blind duplicate split samples to the laboratory, with each specimen identified as a normal field sample; and

(3) including "control" specimens from non-exposed workers.

An evaluation of this data and a comparison of "control" population values to published or unpublished historical "control" data will provide the health practitioners with useful information on laboratory quality and data integrity.

4. URINE DATA - HOW SHOULD THEY BE CORRECTED?

There has been some confusion on how urine data collected as a single voiding "spot" sample should be reported. Most urine data from clinical studies are from 24-hour collections and the results are reported as the amount of analyte excreted per 24 hours. However, urine sampling in an industrial environment does not lead to accurate and uncontaminated 24-hour collections. Logistics, as well as sample integrity, become serious problems. As a result, almost all urine specimens collected for biological monitoring purposes are individual voidings or "spot" specimens collected at a pharmacokinetically correct time following exposure to the environmental contaminant.

The major problem with "spot" urine specimens is the dilution of the urine, as influenced by variations in liquid intake and physical work load. A worker who drinks a large volume of liquids may excrete 500 to 800 mL in a single voiding, whereas a worker who is doing heavy work in a hot environment may excrete less than 100 mL over the same time interval. The absolute amount of metabolite in grams may be identical but concentrations will vary widely. Some attempts at correction of data for the dilution of urine would be desirable to "normalize" the data.

In the past, NIOSH and the industrial hygiene community have utilized a specific gravity correction where the concentration of a urinary analyte would be adjusted to some standardized specific gravity. Usually 1.024 was selected as that standard, although the literature also shows 1.016 and 1.018 as "standards."

It is obvious that urine with a specific gravity of less than 1.010 or greater than 1.035 show rather large corrections — corrections that can change the results by orders of magnitude. Most of these corrections are misleading. Another problem relates to the nature of the specific gravity, i.e., total solids per unit volume. In the case of heavy metal exposure, urinary protein may increase which, when the specific gravity correction is applied, would lead to a falsely low-corrected concentration.

The medical/clinical community has long favored a "normalization" based on the concentration of a normal urinary constituent, creatinine. The substance, a product of tissue breakdown, is excreted at a relatively uniform rate and the total amount excreted per day is quite constant from day-to-day in a given individual. Results are usually expressed as a ratio of the concentration of the analyte divided by the concentration of creatinine in that same urine specimen. Such units are g analyte/g creatinine or mg analyte/g creatinine, etc.

This correction is gaining wide acceptance in the European community and within occupational health circles. Many NIOSH methods in Volumes 1 through 7 of the Second Edition, as well as the First Edition of this Manual, contained specific gravity corrections, creatinine corrections, both corrections or no corrections.

In order to eliminate the confusion, all methods in the Third Edition will show "spot" urine data uncorrected and with the creatinine normalization in line with widespread usage in the recent literature and in the world community. It should be pointed out that a separate creatinine determination is required. No method is included in this manual as most clinical laboratories perform this analysis on multichannel automated analyzers. Manual methods are readily available and most are based on the original Jaffee alkaline picrate method and revisions or adaptions over the years [1].

5. GUIDES TO INTERPRETATION

Interpretation of data is difficult because of the lack of standards or regulations on biological monitoring tests. Results obtained are often dependent on time of collection, specimen integrity, drug or chemical interference, or methodologies. It should be pointed out that finding measurable levels of an occupational chemical in a biological fluid where "normal" people do not have the particular chemical/metabolite carries no adverse health implications in itself. The presence of such chemicals is only an indication of exposure. Further testing or examination of the worker is needed to define health risk.

One recommended approach to data interpretation is to collect specimens from non-exposed control subjects at the workplace and to use this group mean as a baseline to interpret the values from an exposed population. In some cases, a non-exposed control group cannot be obtained from the workplace. In these instances, the use of an outside control group should be considered. Textbooks and literature references are available that quote normal or non-exposed values and some sort of "limit" value [2,3,4,5]. However, caution must be used in applying these numbers to a particular laboratory method and sampling strategy. Some guidance to interpretation is included in each method but any suggested value should not be considered as a NIOSH-recommended limit.

6. REFERENCES

[1] Tietz, Norbert W. Fundamentals of Clinical Chemistry, Second Edition, 994-999, W. B. Saunders Company, Philadelphia, PA (1976).

[2] Lauwerys, Robert R. Industrial Chemical Exposures: Guidelines for Biological Monitoring, Biomedical Publications, Davis, CA (1983).

[3] Baselt, Randall C. Biological Monitoring Methods for Industrial Chemicals, Biomedical Publications, Davis, CA (1980).

[4] Järvisalo, J. and A. Tossavainen. Exposures to Neurotoxic Agents in Finnish Working Environments-Trends and Assessment of Exposure, Occupational Neurology Ed. by J. Juntunen, ACTA Neurologica Scandinavia, Supplementum 92, Vol. 66, 37-46 (1982).

[5] Maximum Concentrations at the Workplace and Biological Tolerance Values for Working Materials 1982, Commission for Investigation of Health Hazards of Chemical Compounds in the Work Area, Report No. XVIII, Deutsche Forschungsgemeinschaft, Verlag Chemie Gmbh, D-6940 Weinhein, 67-72 (in English) (1982).

AIR SAMPLES

FORMULA: CH_3COOH; $C_2H_4O_2$

M.W.: 60.05

ACETIC ACID

METHOD: 1603
ISSUED: 2/15/84

OSHA: 10 ppm
NIOSH: no standard
ACGIH: 10 ppm
(1 ppm = 2.46 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.049 g/mL @ 25 °C;
BP 118 °C; MP 17 °C;
VP 1.5 kPa (11 mm Hg; 1.4% v/v) @ 20 °C;
explosive range 5.4 to 16% v/v in air

SYNONYMS: glacial acetic acid, methane carboxylic acid, ethanoic acid, CAS #64-19-7.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal,
100 mg/50 mg)

FLOW RATE: 0.01 to 1.0 L/min

VOL-MIN: 20 L @ 25 mg/m³
-MAX: 270 L

SAMPLE STABILITY: at least 7 days
@ 25 °C [1,2]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 12.5 to 50 mg/m³ [2]
(173-L samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.058 [2]

MEASUREMENT

!
!TECHNIQUE: GAS CHROMATOGRAPHY, FID
!
!ANALYTE: acetic acid
!
!DESORPTION: 1 mL formic acid; stand 60 min
!
!INJECTION VOLUME: 5 µL
!
!TEMPERATURE-INJECTION: 230 °C
! -DETECTOR: 230 °C
! -COLUMN: 130 to 180 °C, 10°/min
! or 100 °C isothermal

!CARRIER GASES: N_2 or He, 60 mL/min
!
!COLUMN: 1 m x 4 mm ID glass; Carbopack B 60/80
! mesh/3% Carbowax 20M/0.5% H_3PO_4
!
!CALIBRATION: acetic acid in formic acid
!
!RANGE: 0.5 to 10 mg per sample
!
!ESTIMATED LOD: 0.01 mg per sample [3]
!
!PRECISION (s_r): 0.007 [1,2]
!

APPLICABILITY: The working range is 2.5 to 50 mg/m³ for a 200-L air sample. High (90% RH) humidity during sampling did not cause breakthrough at 39 mg/m³ for 4.6 hrs [2].

INTERFERENCES: Formic acid contains a small amount of acetic acid which gives a significant blank value. High purity formic acid must be used to achieve an acceptable detection limit. Alternate columns are 3 m glass, 2 mm ID, 0.3% SP-1000 + 0.3% H_3PO_4 on Carbopack A and 2.4 m x 2 mm ID glass, 0.3% Carbowax 20M/0.1% H_3PO_4 on Carbopack C.

OTHER METHODS: This is Method S169 [1] in a revised format.

REAGENTS:

1. Formic acid, 88%, high purity (0.02% acetic acid).*
   NOTE: The following have been found to have acceptable purity: Fisher 95% formic acid, Malinkrodt 88%, MCB 88%, and Eastman 88% or 95%. The following contained excessive acetic acid: Baker 88%, Fisher 88%, and DuPont 88%.
2. Glacial acetic acid, reagent grade.*
3. Propionic acid, reagent grade.
4. Eluent: Formic acid, 88%, with 0.1% v/v propionic acid or other suitable internal standard.
5. Nitrogen, purified.
6. Hydrogen, prepurified.
7. Air, filtered.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (see page 1603-1).
4. Vials, 2-mL, PTFE-lined caps.
5. Syringes, 10-µL and other convenient sizes for preparing standards, readable to 0.1 µL.
6. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Care should be taken to avoid contacting formic acid and/or acetic acid with the skin. These reagents may cause severe burns.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 1 L/min for a total sample size of 20 to 270 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 60 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.01 to 10 mg acetic acid per sample.
   a. Add known amounts of acetic acid to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg acetic acid).

9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of acetic acid directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg acetic acid recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1603-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with formic acid, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of acetic acid found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of acetic acid in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S169 was issued on May 13, 1977 [1], and validated over the range 12.5 to 50 mg/m^3 at 22 °C and 767 mm Hg using a 173-L sample [2,4]. Overall precision, s_r, was 0.058 with an average recovery of 105.4%, representing a non-significant bias. The concentration of acetic acid was independently verified by a total hydrogen analyzer. Desorption efficiency was 0.96 in the range 2.1 to 8.4 mg per sample. Breakthrough (5% on back section) was never achieved and testing was discontinued after 4.6 hrs when 10.4 mg of acetic acid was collected without breakthrough for a 269-L sample at 90% RH. A user check gave an estimated LOD of 0.01 mg per sample [3].

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd ed., V. 4, S169, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[2] Backup Data Report for Acetic Acid, prepared under NIOSH Contract No. 210-76-0123, available as "Ten NIOSH Analytical Methods," Order No. PB 275-834 from NTIS, Springfield, VA 22161.

[3] User check, UBTL, NIOSH Sequence #4213-K (unpublished, January 31, 1984).
[4] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY: G. David Foley, Y. T. Gagnon, and K. J. Williams, NIOSH/DPSE; S169 originally validated under NIOSH Contract CDC-210-76-0123.

FORMULA: CH_3CN; C_2H_3N

M.W.: 41.06

ACETONITRILE

METHOD: 1606
ISSUED: 2/15/84

OSHA: 40 ppm
NIOSH: 20 ppm [1]
ACGIH: 40 ppm, STEL 60 ppm (skin)
(1.0 ppm = 1.68 mg/m³ @ NTP)

PROPERTIES: liquid; BP 82 °C; d 0.783 g/mL @ 20 °C; VP 12 kPa (89 mm Hg; 12% v/v) @ 25 °C; explosive range 4.4 to 16% v/v in air

SYNONYMS: methyl cyanide; cyanomethane; CAS # 75-05-8.

SAMPLING

METHOD: SOLID SORBENT TUBE
(coconut shell charcoal, 400 mg/200 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 3 L @ 70 mg/m³
-MAX: 25 L

SHIPMENT: routine

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 31.4 to 140.2 mg/m³ [4]
(10-L samples)

BIAS: not significant [4]

OVERALL PRECISION (s_r): 0.072 [4]

MEASUREMENT

!
!TECHNIQUE: GAS CHROMATOGRAPHY, FID
!
!ANALYTE: acetonitrile
!
!DESORPTION: 5-mL benzene; stand 30 min
!
!INJECTION VOLUME: 5.0 µL
!
!TEMPERATURE-INJECTOR: 270 °C
! -DETECTOR: 285 °C
! -COLUMN: 180 °C
!
!CARRIER GAS: N_2 or He, 50 mL/min
!
!COLUMN: stainless steel, 1.2 m x 8 mm O.D., packed with 50/80 mesh Porapak Q
!
!CALIBRATION: solutions of acetonitrile in benzene
!
!RANGE: 0.2 to 2 mg per sample
!
!ESTIMATED LOD: 0.01 mg per sample [2]
!
!PRECISION (s_r): 0.047 [4]
!

APPLICABILITY: Large (400 mg/200 mg) charcoal tubes are necessary for collection of the analyte since breakthrough volume is low with smaller charcoal tubes. The method was used in a NIOSH health hazard evaluation where an estimated limit of detection of 0.01 mg per sample was reported [2]. The capacity of the charcoal for the analyte has not been determined under conditions of high relative humidity [4].

INTERFERENCES: None identified.

OTHER METHODS: This is Method S165 [3] in a revised format.

REAGENTS:

1. Acetonitrile, chromatographic quality.
2. Benzene, chromatographic quality.*
3. Calibration stock solution, 70 mg/mL. Add 700 mg (0.894 mL) acetonitrile to a 10-mL volumetric flask. Dilute to the mark with benzene.*
4. Nitrogen, purified.
5. Hydrogen, pre-purified.
6. Air, filtered.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 9.0 cm long, 8 mm OD, 6 mm ID; two sections of 20/40 mesh activated (600 °C) coconut charcoal (front = 400 mg, back = 200 mg), separated by a 3-mm section of urethane foam and held in place with plugs of silanized glass wool, flame-sealed at both ends; plastic caps for tube.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1606-1).
4. Vials, glass, 10-mL, PTFE-lined crimp caps.
5. Syringes, 10- to 50-µL, readable to 0.1 µL; 1.0-mL, readable to 0.01 mL.
6. Volumetric flasks, 10-mL.
7. Pipets, delivery-type, 5.0-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Benzene is a suspected human carcinogen. Perform all work with this solvent in a hood.

NOTE: Solutions of the analyte may be prepared in a less toxic solvent such as toluene; however, this approach has not been evaluated.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 3 to 25 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 5.0 mL benzene to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.01 to 2 mg acetonitrile per sample.
   a. Add known amounts of calibration stock solution to benzene in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg acetonitrile).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.

a. Remove and discard back sorbent section of a media blank sampler.
b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg acetonitrile recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1606-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with benzene, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of acetonitrile found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of acetonitrile in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD [4]:

Method S165 was issued on August 1, 1975 [3]. Synthetic atmospheres of the analyte in dry air were generated dynamically at 22 °C and 762 torr by the vapor pressure saturation/air dilution technique [4]. The concentrations ranged from 31.4 to 140.2 mg/m³; these were verified by total hydrocarbon analyzer. Mean recovery was 105%. Breakthrough of the 400-mg front sorbent section occurred after sampling 140 mg/m³ for 190 min at 0.196 L/min (37.2 L). The desorption efficiency, over the range 0.346 to 1.383 mg per sample, averaged 81%. A DE correction factor was used to compute the total recovery of the collected samples. Recovery of the analyte after long-term storage on the sorbent was not evaluated.

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Nitriles, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-212 (1978).
[2] NIOSH Health Hazard Evaluation Report HHE 81-359-1058 (1981).
[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3, S165, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[4] Documentation of the NIOSH Validation Tests, S165, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).

METHOD REVISED BY: Robert Glaser, NIOSH/DPSE; S165 originally validated under NIOSH Contract CDC-99-74-45.

FORMULA: (1) HF (4) HBr
(2) HCl (5) HNO_3
(3) H_3PO_4 (6) H_2SO_4

ACIDS, INORGANIC

METHOD: 7903
ISSUED: 2/15/84

OSHA/NIOSH/ACGIH: Table 1

PROPERTIES: Table 1

SYNONYMS: (1) hydrofluoric acid; hydrogen fluoride; CAS #7664-39-3.
(2) hydrochloric acid; hydrogen chloride; CAS #7647-01-0.
(3) phosphoric acid; ortho-phosphoric acid; meta-phosphoric acid; CAS #7664-38-2.
(4) hydrobromic acid; hydrogen bromide; CAS #10035-10-6.
(5) nitric acid; aqua fortis; CAS #7697-37-2.
(6) sulfuric acid; oil of vitriol; CAS #7664-93-9.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(washed silica gel, 400 mg/200 mg
with glass fiber filter plug)

FLOW RATE: 0.2 to 0.5 L/min

VOL-MIN: 3
-MAX: 100

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD

BIAS: not significant [2,3,6]

OVERALL PRECISION (s_r): see EVALUATION OF METHOD

MEASUREMENT

TECHNIQUE: ION CHROMATOGRAPHY

ANALYTE: F^-, Cl^-, PO_4^{3-}, Br^-, NO_3^-, SO_4^{2-}

DESORPTION: 10 mL 3 mM $NaHCO_3$/2.4 mM Na_2CO_3

INJECTION LOOP VOLUME: 100 µL

ELUENT: 3 mM $NaHCO_3$/2.4 mM Na_2CO_3; 3 mL/min

COLUMNS: anion separator, fast run; anion precolumn, fast run; anion suppressor

CONDUCTIVITY SETTING: 10 µS full scale

RANGE: see EVALUATION OF METHOD

ESTIMATED LOD: see EVALUATION OF METHOD

PRECISION (s_r): see EVALUATION OF METHOD

APPLICABILITY: The working range is ca. 0.01 to 5 mg/m³ for a 50-L air sample (see EVALUATION OF METHOD). This method measures the total concentration of six airborne anions. The corresponding acids may be collected on a single sampler and determined simultaneously.

INTERFERENCES: Particulate salts of all the acids will give a positive interference. Chlorine or hypochlorite ion interfere with chloride determination and bromine interferes with bromide. Collection efficiency of Br_2 and Cl_2 on silica gel has not been investigated. Acetate, formate and propionate have elution times similar to F^- and Cl^-. If these anions are present, use a weak eluent (e.g., 1.5 mM $NaHCO_3$) in the IC for greater resolution.

OTHER METHODS: This is P&CAM 339 in a revised format [1]. Alternate methods are 7902 for fluoride and P&CAM 268 for sulfate [5].

51 Preceding page blank

REAGENTS:

1. Silica gel, 20/40 mesh, grade 01, thoroughly washed with deionized water (see APPENDIX).
2. Distilled, deionized water, filtered through 0.45-µm membrane filter.
3. Eluent: bicarbonate/carbonate buffer solution (3 mM $NaHNO_3$/ 2.4 mM Na_2CO_3). Dissolve 1.008g $NaHCO_3$ and 1.018 g Na_2CO_3 in 4 L filtered deionized water.
4. Calibration stock solutions, 1 mg/mL (as the anion). Dissolve salt in filtered deionized water.
   a. Fluoride: 0.2210 g NaF/100 mL.
   b. Chloride: 0.2103 g KCl/100 mL.
   c. Phosphate: 0.1433 g KH_2PO_4/100 mL.
   d. Bromide: 0.1288 g NaBr/100 mL.
   e. Nitrate: 0.1371 g $NaNO_3$/100 mL.
   f. Sulfate: 0.1814 g K_2SO_4/100 mL.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 11 cm x 7 mm OD, containing a 400-mg front section and 200-mg backup section of washed silica gel. Front section is retained with a glass fiber filter plug. Urethane plugs separate and retain the backup section. Tubes are commercially available (Supelco Orbo 53 or equivalent) or may be prepared according to APPENDIX.
2. Personal sampling pump, 0.2 to 0.5 L/min, with flexible connecting tubing.
3. Ion chromatograph, fast-run anion separator and precolumn, anion suppressor column, conductivity detector, integrator and strip chart recorder.
4. Waterbath: hotplate with beaker of boiling water.
5. Centrifuge tubes, 15-mL, graduated, plastic, with caps.*
6. Syringes, 10-mL, polyethylene with luer tip.
7. Filters, luer tip, with membrane filter, 13-mm, 0.8-µm pore size.
8. Micropipettes, disposable tips.
9. Volumetric flasks, 50- and 100-mL.*
10. Laboratory timer.
11. Bottles, polyethylene, 100-mL.

*See Special Precautions.

SPECIAL PRECAUTIONS: Acids, particularly HF, are extremely corrosive to skin, eyes, and mucous membranes. HF will attack glass. Plastic labware is recommended.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.2 and 0.5 L/min for a total sample size of 3 to 100 L.
   NOTE: Do not exceed 0.3 L/min when sampling for HF.

SAMPLE PREPARATION:

4. Score sampler with a file in front of primary sorbent section.
5. Break sampler at score line. Transfer glass fiber filter plug and primary sorbent section to a 15-mL graduated centrifuge tube.
6. Place backup sorbent section in separate centrifuge tube. Discard urethane plugs.
7. Add 6 to 8 mL eluent to each centrifuge tube. Heat in boiling waterbath for 10 min.
   NOTE: Eluent used for desorption should be from same batch as the eluent used on the chromatograph to avoid carbonate/bicarbonate peaks near F^- and Cl^-.
8. Allow to cool, dilute to 10.0-mL volume with eluent.
9. Cap the centrifuge tube and shake vigorously.
10. Pour sample into 10-mL plastic syringe fitted with in-line filter.

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with at least five working standards covering the range 0.001 to 0.3 mg of each anion per sample.
    a. Add known aliquots of calibration stock solution to eluent in 50-mL volumetric flasks and dilute to the mark.
    b. Store working standards in tightly-capped polyethylene bottles. Prepare fresh working standards weekly.
    c. Analyze working standards together with samples and blanks (steps 12 through 14).
    d. Prepare a calibration graph for each anion [peak height (mm or µS) vs. mg].

MEASUREMENT:

12. Set ion chromatograph to conditions give on page 7903-1, according to manufacturer's instructions.
13. Inject 100-µL sample aliquot. For manual operation, inject 2 to 3 mL of sample from filter/syringe to ensure complete rinse of sample loop.
    NOTE: All samples, eluents and water flowing through the IC must be filtered to avoid plugging system valves or columns.
14. Measure peak height.
    NOTE: If sample peak height exceeds linear calibration range, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.

CALCULATIONS:

15. Determine the mass, mg, of anion found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
16. Calculate concentration, C, of acid in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3 \cdot F}{V}, \text{ mg/m}^3$$

where: F (conversion factor from anion to acid) = 1.053 for HF; 1.028 for HCl; 1.032 for H_3PO_4; 1.012 for HBr; 1.016 for HNO_3; and 1.021 for H_2SO_4.

EVALUATION OF METHOD:

The method was evaluated for hydrochloric, hydrobromic, nitric, phosphoric and sulfuric acids by laboratory generation of mixed acids [2]. Data for the individual analytes are:

Acid	Range Studied (mg/m³)	Range Studied (µg/sample)	Measurement Precision (s_r)	Overall Precision (s_r)	Estimated LOD (µg per sample)
HF [6]	0.35 - 6	0.5 - 200	0.053	0.116	1
HCl [3]	0.14 - 14	0.5 - 200	0.025	0.059	2
H_3PO_4 [2]	0.5 - 2	3 - 100	0.029	0.096	2
HBr [2]	2 - 20	3 - 960	0.056	0.074	1
HNO_3 [2]	1 - 10	3 - 500	0.018	0.085	1
H_2SO_4 [2]	0.5 - 2	3 - 100	0.028	0.087	4

The method was field-evaluated at two electroplating facilities using side-by-side silica gel tubes and bubblers. The method was evaluated for hydrofluoric acid in 1983 using the silica gel tubes and impingers [6]. Recovery based on impinger collection was 106% with s_r of 0.116. The capacity of the silica gel sampler for HF was 820 µg. This is equivalent to an 8-hr sample at two to three times the OSHA PEL. Samples were stable for at least 21 days at 25 °C.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd. ed., V. 7, P&CAM 339, U.S. Department of Health and Human Services, Publ. (NIOSH) 82-100 (1982).
[2] Cassinelli, M. E. and D. G. Taylor. Airborne Inorganic Acids, ACS Symposium Series 149, 137-152 (1981).
[3] Cassinelli, M. E. and P. M. Eller. Ion Chromatographic Determination of Hydrogen Chloride, Abstract No. 150, American Industrial Hygiene Conference, Chicago, IL (1979).
[4] NIOSH Manual of Analytical Methods, 2nd. ed., V. 5, P&CAM 310, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[5] Ibid, P&CAM 268.
[6] Cassinelli, M. E. Hydrogen Fluoride Report (in preparation).

METHOD WRITTEN BY: Mary Ellen Cassinelli, NIOSH/DPSE.

APPENDIX:

SAMPLING TUBE PREPARATION

Silica gel cleaning procedure: Add 500 to 600 mL deionized water, slowly and with stirring, to ca. 200 mL volume of silica gel in 1-L beaker. When exothermal reaction has subsided, heat in boiling waterbath for ca. 30 min with occasional stirring. Decant and rinse four to five times with deionized water. Repeat cleaning procedure and dry overnight in 100 °C oven until free flowing. If blank of silica gel shows impurities, repeat cleaning procedure.

Silica gel tubes: Pack glass tubes, 7 mm OD, 4.8 mm ID, 11 cm long, with 400 mg of 20/40 mesh washed silica gel in front section and 200 mg backup section. Use urethane foam plugs between sorbent sections and at back end. Hold front section in place with 6-mm diameter, 1-mm thick glass fiber filter plug (Gelman 66088).

Table 1. General information.

Acid and M.W.	EXPOSURE LIMITS (ppm) OSHA	NIOSH	ACGIH	mg/m³ = 1 ppm @ NTP	PROPERTIES Physical State	MP (°C)	BP (°C)	Sp. Gr. (liq.)	VP @ 20 °C kPa (mm Hg)
HF (20.01)	3	3; 6/15 min	3; STEL 6	0.818	gas	-83.1	19.5	0.987	>101 (>760)
HCl (36.46)	C 5	--	C 5	1.491	gas	-114.8	-85.0	1.194	>101 (760)
H_3PO_4 (97.99)	1 mg/m³	--	1 mg/m³; STEL 3 mg/m³	4.01	liquid	21.0	260	1.7	0.0038 (0.03)
HBr (80.92)	3	--	3	3.31	gas	-88.5	-66.8	2.16	>101 (>760)
HNO_3 (63.01)	2	2	2; STEL 4	2.58	liquid	-42.0	83	1.50	0.39 (2.9)
H_2SO_4 (98.08)	1 mg/m³	1 mg/m³	1 mg/m³	--	liquid	3.0	290	1.84	<0.0001 (<0.001)

FORMULA: $H_2C=CHCHO$; C_3H_4O

M.W.: 56.07

ACROLEIN

METHOD: 2501
ISSUED: 2/15/84

OSHA: 0.1 ppm
NIOSH: no standard
ACGIH: 0.1 ppm; STEL 0.3 ppm
(1 ppm = 2.5 mg/m³ @ NTP)

PROPERTIES: liquid; d 0.8389 @ 20 °C;
BP 52.5 °C; MP -88 °C;
VP 28.5 kPa (214 mm Hg; 28% v/v) @ 20 °C
explosive range 2.8 to 31% v/v in air

SYNONYMS: 2-propenal; acraldehyde; CAS #107-02-8.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(2-(hydroxymethyl)piperidine on XAD-2, 120 mg/60 mg)

FLOW RATE: 0.01 to 0.1 L/min

VOL-MIN: 1.5 L
-MAX: 48 L

SHIPMENT: routine

SAMPLE STABILITY: at least 4 weeks @ 25 °C

BLANKS: 2 to 10 field blanks and 10 media blanks per set

ACCURACY

RANGE STUDIED: 0.12 to 1.50 mg/m³
(24-L samples)

BIAS: not significant

OVERALL PRECISION (s_r): 0.111

MEASUREMENT

!
!TECHNIQUE: GAS CHROMATOGRAPHY, NITROGEN-SPECIFIC
! DETECTOR
!
!ANALYTE: 9-vinyl-1-aza-8-oxabicyclo[4.3.0]nonane
!
!DESORPTION: 2 mL toluene; place in ultrasonic
! bath for 30 min
!
!INJECTION VOLUME: 1 µL
!
!TEMPERATURE-INJECTION: 230 °C
! -DETECTOR: 250 °C
! -COLUMN: 90 °C for 8 min;
! 20 °C/min; hold @ 200 °C
! for 11 min
!
!CARRIER GAS: Helium, 30 mL/min
!
!COLUMN: 2 m x 2 mm glass, 5% SP-2401-DB on
! Supelcoport (100-120 mesh)
!
!CALIBRATION: acrolein spiked on coated sorbent
!
!RANGE: 3 to 36 µg per sample
!
!ESTIMATED LOD: 2 µg per sample
!
!PRECISION (s_r): not determined
!

APPLICABILITY: The method has sufficient sensitivity for personal monitoring below the PEL of 0.1 ppm with an 8 hr sample collected at 0.10 L/min. For STEL measurements, the limit of the method is 0.8 ppm for a 15 min sample.

INTERFERENCES: None known. Peaks for acetaldehyde and formaldehyde oxazolidines may be observed in the chromatogram, but they are resolved from the acrolein peak. Capacity of the sampler is reduced if sampling in air containing acids.

OTHER METHODS: This method was developed to give improved sample stability and to provide for ease of personal sampling compared to P&CAM 118 [1] and P&CAM 211 [1], which have not been revised.

REAGENTS:

1. Toluene, chromatography quality.
2. Acrolein,* freshly distilled under N_2 to remove stabilizer. Store at 0 °C.
3. 2-(Hydroxymethyl)piperidine. Recrystallize several times from isooctane until pure by GC analysis. Store in dessicator.
4. XAD-2 (Amberlite - Rohm and Haas) or equivalent. Extract 4 hrs in soxhlet with 50/50 (v/v) acetone/methylene chloride. Replace with fresh solvent and repeat. Vacuum dry overnight.
5. Calibration stock solution, 1.0 µg/µL. Add 11.9 µL acrolein to a septum-capped 10-mL toluene.

*See Special Precautions.

EQUIPMENT:

1. Sampling tube: glass tube, 10 cm x 4 mm ID, containing a 120-mg front section and a 60-mg back-up section of the 2-(hydroxymethyl)piperidine-coated XAD-2 (see APPENDIX) with flame-sealed ends. Sorbent sections are retained and separated by small plugs of silanized glass wool. Pressure drop ca. 2.2 inches of water (756 Pa) at 0.10 L/min. Tubes are commercially available (Supelco ORBO 23 or equivalent).
2. Sampling pump, 0.02 to 0.1 L/min, with flexible connecting tubing.
3. Vials, 4-mL, with septum and plastic screw caps.
4. Ultrasonic bath.
5. Pipettes, volumetric, 1- and 2-mL, with pipet bulb.
6. Flasks, volumetric, 10-mL.
7. Pipettes, disposable, 2-mL.
8. Syringes, 10-µL (readable to 0.1 µL) and 25- and 50-µL.
9. Gas chromatograph, nitrogen-specific detector, integrator and column (page 2501-1).
10. File.

SPECIAL PRECAUTIONS: Acrolein is an acute irritant and a potential fire hazard (flash point = -17.8 °C); work with this compound only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Score and break the ends of the sampler with a file immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.1 L/min for a total sample size of 1.5 to 48 L.

   NOTE: Sampling rate is limited by the speed of reaction of acrolein with the sorbent coating. Sampling at rates above 0.10 L/min could cause appreciable acrolein breakthrough, possibly invalidating the sample.

SAMPLE PREPARATION:

4. Score each sampler with a file in back of the rear sorbent section.
5. Break sampler at score line. Remove and place glass wool plug and rear sorbent section in a 4-mL vial.
6. Transfer front section with the remaining glass wool plugs to a second 4-mL vial.
7. Add 2.0 mL of toluene to each vial. Screw cap tightly onto each vial.
8. Agitate vials by placing them in an ultrasonic bath for 30 min.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least five standards covering the range of the samples.
   a. Weigh ten 120-mg portions of the coated sorbent into 4-mL vials with septum caps. If the bulk coated sorbent is not available, remove the front section from 10 unused samplers (media blanks).

b. Inject aliquots of the calibration stock solution into the vials at five different levels and allow to sit overnight at room temperature. Prepare duplicate standards at each level.
c. Analyze together with samples and blanks (steps 7, 8, 10 and 11).
d. Prepare calibration graph (peak area or height vs. concentration of acrolein, µg/mL).
NOTE: The calibration procedure used in this method does not require a desorption efficiency (DE) correction to be made. If DE is needed, see the APPENDIX.

MEASUREMENT:

10. Set gas chromatograph to conditions given on page 2501- 1. Set air and hydrogen flows on the nitrogen specific detector to manufacturer's specifications. Inject 1-µL sample aliquot.
11. Measure peak area or peak height. t_r for acrolein derivative = 3.6 min and t_r for 2-(hydroxymethyl)piperidine = 10.7 min for these conditions.

CALCULATIONS:

14. Read the µg/mL of acrolein found in the sample front (W_f) and back (W_b) sorbent sections from the calibration graph and multiply by the desorption volume, 2 (mL). Calculate concentration, C (mg/m^3), of acrolein in the air volume sampled, V (L):
NOTE: Because the working standards are prepared on media blanks, no additional blank correction is necessary.

$$C = \frac{(W_f + W_b) \cdot 2}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

The method was evaluated over the range of 0.12 to 1.5 mg/m^3 using 24-L samples. Average desorption efficiencies were ca. 1.0 for all levels studied. Recovery was essentially 100%, representing no bias in the method. Concentration of the generated acrolein vapor was independently verified by a modification of P&CAM 211 by Shell Development Co. [2]. No breakthrough was observed for an 8-hr sample at 0.10 L/min (48 L) of a 4.5 mg/m^3 of acrolein at 80% RH. The method has been used by three separate analysts at NIOSH and no intralaboratory variability was observed.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd ed., V. 1, P&CAM 118 and 211, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[2] Shell Development Company Analytical Department. Determination of Acrolein in Air, Bubbler/Colorimetric Method, SRC 11A11/79, Shell Development Company Westhollow Research Center.

METHOD WRITTEN BY: Eugene R. Kennedy, Ph.D. and Paula Fey O'Connor, NIOSH/DPSE.

APPENDIX:

SORBENT PREPARATON

Add 1 g of the purified 2-(hydroxymethyl)piperidine in 50 mL of toluene for each 9 g of extracted XAD-2 sorbent . Allow this mixture to stand for 1 hr with occasional swirling. Remove the solvent by rotary evaporation at 37 °C and dry at 130 Pa (1 mm Hg) at ambient temperature for approximately 1 hr. To determine the amount of background for each batch, desorb several 120-mg portions of the coated sorbent with toluene and analyze using steps 6 through 11. No blank peak is expected for acrolein although a blank for formaldehyde and acetaldehyde may be observed.

DESORPTION EFFICIENCY

The determination of desorption efficiency (DE) is not necessary when using the calibration procedure outlined in this method. The following procedure can be used to determine DE, if necessary:

a. Using a 10-µL syringe and the calibration stock solution inject four sampling tubes at each of five levels. Open several blank tubes but add no acrolein to them. Cap all the tubes.
b. Using the 10-µL syringe, spike the calibration stock solution into 4-mL vials containing 2 mL of toluene and 10 mg of purified 2-(hydroxymethyl)piperidine. Prepare four replicate vials at each of the five concentrations used in step a.
c. Allow the spiked tubes, spiked standard solutions and blank tubes to sit overnight at ambient temperature to assure complete reaction. Desorb and analyze the spiked and blank tubes according to steps 4 through 11. Analyze the spiked solutions according to steps 10 and 11.
d. To calculate the recovery, compare the blank-corrected peak areas or heights of the acrolein peak found in the spiked tubes (Q_r - B) to the peak area or height of the acrolein peak found in the spiked solutions (Q_a).

$$DE = \frac{Q_r - B}{Q_a}.$$

Prepare a graph of DE vs. µg acrolein recovered.

FORMULA: CH_2=CHCN; C_3H_3N

M.W.: 53.06

ACRYLONITRILE

METHOD: 1604
ISSUED: 2/15/84

OSHA: 2 ppm; C 10 ppm (skin)
NIOSH: 4 ppm/4 hr TWA [1]
ACGIH: 2 ppm (skin)
(1 ppm = 2.17 mg/m³ @ NTP)

PROPERTIES: liquid; sp. gr. 0.8004 (25 °C);
BP 77.2 °C;
VP 11 kPa (83 mm Hg; 11% v/v) @ 20 °C
explosive range 3 to 17% v/v in air

SYNONYMS: 2-propenenitrile; vinyl cyanide; CAS #107-13-1.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 4 L @ 2 ppm
-MAX: 20 L

SHIPMENT: routine

SAMPLE STABILITY: at least 8 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: none identified

OVERALL PRECISION (s_r): not evaluated

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: acrylonitrile

DESORPTION: 1 mL 2% (v/v) acetone in CS_2;
stand 30 min

INJECTION VOLUME: 2 µL

TEMPERATURE-INJECTOR: 200 °C
-DETECTOR: 200 °C
-COLUMN: 85 °C

CARRIER GAS: N_2 or He, 25 mL/min

COLUMN: 3 m x 3 mm stainless steel, 20% SP-1000 on 80/100 Supelcoport or equivalent

RETENTION TIME: ca. 8.6 min

CALIBRATION: solutions of distilled acrylonitrile in hexane

RANGE: 0.015 to 1 mg per sample

ESTIMATED LOD: 0.001 mg per sample

PRECISION (s_r): 0.06 [5]

APPLICABILITY: The working range is 0.5 to 31 ppm (1 to 67 mg/m³) for a 15-L air sample. NIOSH has sampled for acrylonitrile at acrylic and electric plants.

INTERFERENCES: None known.

OTHER METHODS: This method revises and replaces Method S156 [1,2]. P&CAM 202 has been dropped because of poor sensitivity (LOD 0.1 mg per sample) [3].

REAGENTS:

1. Carbon disulfide, chromatographic quality.*
2. Acetone, chromatographic quality.
3. Hexane, reagent grade.
4. Eluent: 2% acetone (v/v) in carbon disulfide.
5. Acrylonitrile, stabilized.* Stable at least one month at 4 °C.
6. Acrylonitrile, freshly distilled.*
7. Calibration stock solution, 4 µg/µL. Add 50 µL freshly distilled acrylonitrile to 10 mL hexane. Stable one week at 4 °C.
8. Helium, purified.
9. Hydrogen, prepurified.
10. Air, filtered.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg, back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 1604-1).
4. Micro-distillation apparatus for vacuum distillation of acrylonitrile.
5. Vials, 2-mL, PTFE-lined crimp caps.
6. Syringe, 10-µL and other sizes as needed, readable to 0.1 µL.
7. Volumetric flasks, 10-mL.
8. Pipets, 1-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); work with it only in a hood.

Acrylonitrile is explosive, flammable, toxic and a suspect carcinogen [1]. Work with these compounds only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 4 to 20 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.001 to 1 mg acrylonitrile per sample.
   a. Add known amounts of calibration stock solution to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).

c. Prepare calibration graph (peak area vs. mg acrylonitrile).
NOTE: Compare the peak areas of the working standards with a 0.1 mg/mL reference standard prepared from stabilized (undistilled) acrylonitrile in hexane. When the concentration of the working standards starts to decrease, prepare new working standards.

9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg acrylonitrile recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1604-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of acrylonitrile found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of acrylonitrile in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S156 [2] was issued on July 4, 1975, and validated at levels of 8.6 and 16.6 µg per sample, using samples prepared both by sampling acrylonitrile from standard atmospheres prepared by calibrated syringe drive and by application of aliquots of a standard solution of acrylonitrile in hexane to the charcoal [4]. At the higher levels, the recoveries of acrylonitrile averaged 94% and the s_r was 0.06. At the lower level, the recovery for the two sets of samples prepared from standards atmospheres averaged 79% with a s_r of 0.14. The set prepared from the standard solution had a recovery of 94% suggesting a possible problem with accuracy at this level [5]. Samples appear to be stable for at least seven days at room temperature [4,5]. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 100 mg of charcoal) reaches 5% of the concentration in the test mixture. Several breakthrough studies have been done. At 80% relative humidity, breakthrough occurred after 184 min (36.7 L) sampling 8 mg/m³ at 0.2 L/min [6]. Breakthrough did not occur after sampling dry air at 92 mg/m³ at 0.2 L/min for 4 hrs [4].

REFERENCES:
[1] Criteria for a Recommended Standard...Occupational Exposure to Acrylonitrile, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-116 (1977).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3, S156, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[3] Ibid, V. 1, P&CAM 202, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[4] Documentation of the NIOSH Validation Tests, S156, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[5] Posner, J. C. Recovery of Acrylonitrile from Charcoal Tubes at Low Levels, Am. Ind. Hyg. Assoc. J., 40, 923-925 (1979).
[6] OSHA Report, Acrylonitrile Method 37, Organic Methods Evaluation Branch, OSHA Analytical Laboratory, Salt Lake City, UT (May, 1982).

METHOD REVISED BY: Y. T. Gagnon, NIOSH/DPSE; S156 originally validated under NIOSH Contract CDC-99-74-45.

FORMULA: Table 1

M.W.: Table 1

ALCOHOLS I

METHOD: 1400
ISSUED: 2/15/84

OSHA/NIOSH/ACGIH: Table 1

PROPERTIES: Table 1

COMPOUNDS AND SYNONYMS: (1) ethanol: [ethyl alcohol; CAS #64-17-5];
(2) isopropyl alcohol: [2-propanol; CAS #67-63-0]; and
(3) tert-butyl alcohol: [2-methyl-2-propanol; CAS #75-65-0].

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min
(0.05 L/min for ethyl alcohol)

	(1)	(2)	(3)
VOL-MIN:	0.1 L	0.2 L	0.5 L
-MAX:	1 L	3 L	10 L

SHIPMENT: refrigerated

SAMPLE STABILITY: store in freezer; analyze as sooh as possible

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD

BIAS: not significant [1]

OVERALL PRECISION (s_r): see EVALUATION OF METHOD

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 1 mL 1% 2-butanol in CS_2

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 250 - 300 °C
-COLUMN: 65 - 70 °C

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: glass, 2 m x 4 mm ID, 0.2% Carbowax 1500 on 60/80 Carbopack C or equivalent

CALIBRATION: solutions of analyte in eluent with internal standard

RANGE AND PRECISION: see EVALUATION OF METHOD

ESTIMATED LOD: 0.01 mg per sample [4]

APPLICABILITY: This method employs a simple desorption and may be used to determine two or more analytes simultaneously by varying GC conditions (e.g., temperature programming).

INTERFERENCES: High humidity reduces sampling efficiency. The methods were validated using a 3 m x 3 mm stainless steel column packed with 10% FFAP on Chromosorb W-AW; other columns with equal or better resolution (e.g., capillary) may be used. Less volatile compounds may displace more volatile compounds on the charcoal.

OTHER METHODS: This method combines and replaces Methods S56, S65 and S63 [3].

REAGENTS:

1. Eluent: Carbon disulfide* (chromatographic grade) with 1% (v/v) 2-butanol and 0.2% v/v n-undecane, 0.1% v/v ethyl benzene, or other suitable internal standard.
2. Analyte, reagent grade.
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, compressed, filtered.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1400-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); all work with it must be done in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 0.1 to 1 L (ethanol), 0.2 to 3 L (isopropyl alcohol) or 0.5 to 10 L (t-butyl alcohol).
4. Cap the samplers with plastic (not rubber) caps and pack securely with bagged refrigerant for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.01 to 6 mg analyte per sample.
   a. Add known amounts of analyte to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.

b. Inject a known amount of analyte directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg analyte recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1400-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Methods S56, S65 and S63 were issued on January 17, 1975 [3], and validated using 1-, 3- and 10-L air samples, respectively, of atmospheres generated in dry air by calibrated syringe drive from absolute ethanol, 2-propanol and t-butyl alcohol [1]. Overall precision and recovery were as shown below, representing non-significant bias in each method:

Method	Overall Precision (s_r)	Recovery (%)	Range Studied		Breakthrough @ 2X OSHA	Avg. DE	Measurement Precision (s_r)
			mg/m³	mg per sample			
S56	0.065	103.6	900 to 3300	1 to 4	1.6 L	0.79*	0.027
S65	0.064	96.7	505 to 1890	1 to 5	6.0 L	0.93*	0.033
S63	0.075	100.3	165 to 600	1.5 to 6	17.0 L	0.91*	0.018

*Over the range studied. Each laboratory must do their own DE determinations.

REFERENCES:
[1] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, (NIOSH) Publication No. 77-185 (1977).
[2] White, L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Am. Ind. Hyg. Assoc. J., 31:225 (1970).
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 2., S56, S65 and S63, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[4] User check, UBTL, NIOSH Sequence #3990-S (unpublished, November 3, 1983).

METHOD REVISED BY: George Williamson, NIOSH/DPSE; methods originally validated under NIOSH Contract 99-74-45.

Table 1. General information.

Compound	OSHA NIOSH ACGIH (ppm)	Formula	mg/m³ = 1 ppm @ NTP	M.W.	Density @ 20 °C (g/mL)	BP (°C)	VP @ 20 °C, kPa (mm Hg)
Ethanol	1000 -- 1000	CH_3CH_2OH; C_2H_6O	1.883	46.07	0.789	78.5	5.6 (42)
Isopropyl alcohol	400 400 500	$CH_3CH(OH)CH_3$; C_3H_8O	2.46	60.09	0.785	82.5	4.4 (33)
tert-Butyl alcohol	100 100 150	$(CH_3)_3COH$; $C_4H_{10}O$	3.03	74.12	0.786	82.4; MP = 25.6 °C	4.1 (31)

FORMULA: Table 1

M.W.: Table 1

ALCOHOLS II

METHOD: 1401
ISSUED: 2/15/84

OSHA/NIOSH/ACGIH: Table 1

PROPERTIES: Table 1

COMPOUNDS (1) n-butyl alcohol: [1-butanol; CAS #71-36-3];
and (2) sec-butyl alcohol: [2-butanol; CAS #78-92-2];
SYNONYMS: (3) isobutyl alcohol: [2-methyl-1-propanol; CAS #78-83-1]; and
(4) n-propyl alcohol: [1-propanol; CAS #71-23-8].

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L
-MAX: 10 L

SHIPMENT: routine

SAMPLE STABILITY: unknown; store in freezer

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD

BIAS: not significant [1]

OVERALL PRECISION (s_r): see EVALUATION OF METHOD

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 1 mL 1% 2-propanol in CS_2

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 250 - 300 °C
-COLUMN: 75 °C

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: glass, 3 m x 2 mm ID, 10% SP-1000 on 80/100 mesh Chromosorb WHP, or equivalent

CALIBRATION: solutions of analyte in eluent with internal standard

RANGE AND PRECISION: see EVALUATION OF METHOD

ESTIMATED LOD: 0.01 mg per sample [2]

APPLICABILITY: The working range is ca. 50 to 900 mg/m^3 of each analyte for a 10-L air sample. This method may be used to determine two or more analytes simultaneously by varying GC conditions (e.g., temperature programming).

INTERFERENCES: The methods were validated using a 3 m x 3 mm ID stainless steel column packed with 10% FFAP on Chromosorb W-AW; other columns with equal or better resolution (e.g., capillary) may be used.

OTHER METHODS: This method combines and replaces Methods S66, S53, S64 and S62 [3].

71 Preceding page blank

REAGENTS:

1. Eluent: Carbon disulfide* (chromatographic grade) with 1% (v/v) 2-propanol and 0.2% (v/v) n-undecane, 0.1% (v/v) hexane or other suitable standard.
2. Analyte.
3. DE stock solution, 100 mg/mL. Prepare solutions of each analyte in heptane.
4. Nitrogen, purified.
5. Hydrogen, prepurified.
6. Air, compressed, filtered.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1401-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); all work with it must be done in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 1 to 10 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.1 to 10 mg analyte per sample.
   a. Add known amounts of analyte to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of DE stock solution directly onto front sorbent section with a microliter syringe.

c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg analyte recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1401-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Methods S66 (n-butyl alcohol), S53 (sec-butyl alcohol), S64 (isobutyl alcohol), and S62 (n-propyl alcohol) were issued on January 17, 1975, and validated using 10-L air samples of atmospheres generated by injection of the pure alcohol into dry air using a calibrated syringe drive [1]. Overall precision and recovery were as shown below, representing non-significant bias in each method:

Method	Overall Precision (s_r)	Recovery (%)	Range Studied		Breakthrough @ 2X OSHA in Dry Air	Avg. DE	Measurement Precision (s_r)
			mg/m³	mg per sample			
S66	0.065	100.0	170 to 610	1.5 to 6	35 L	0.89	0.021
S53	0.066	107.2	270 to 850	2.2 to 9	15 L	0.92	0.028
S64	0.073	100.0	180 to 620	1.5 to 6	31 L	0.85	0.023
S62	0.075	103.5	225 to 835	2.5 to 10	19 L	0.89	0.016

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] User check, UBTL, NIOSH Sequence #3990-X (unpublished, November 3, 1983).
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 2., U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

METHOD REVISED BY: George Williamson, NIOSH/DPSE; S53, S62, S64 and S66 originally validated under NIOSH Contract 99-74-45.

Table 1. General information.

Compound	Exposure Limits, OSHA NIOSH ACGIH (ppm)	Formula	mg/m³ = 1 ppm @ NTP	M.W.	Density (g/mL)	BP (°C)	VP @ 20 °C, kPa (mm Hg)
n-Butyl alcohol	100 — C 50 (skin)	$CH_3CH_2CH_2CH_2OH$; $C_4H_{10}O$	3.03	74.12	0.810 @ 20 °C	117	0.56 (4.2)
sec-Butyl alcohol	150 — 100	$CH_3CH(OH)CH_2CH_3$; $C_4H_{10}O$	3.03	74.12	0.808 @ 20 °C	99.5	1.7 (13)
Isobutyl alcohol	100 — 50	$(CH_3)_2CHCH_2OH$; $C_4H_{10}O$	3.03	74.12	0.806 @ 15 °C	108	1.2 (9)
n-Propyl alcohol	200 — 200 (skin)	$CH_3CH_2CH_2OH$; C_3H_8O	2.46	60.09	0.805 @ 20 °C	97	2.0 (15)

FORMULA: Table 1

M.W.: Table 1

ALCOHOLS III

METHOD: 1402
ISSUED: 2/15/84

OSHA/NIOSH/ACGIH: Table 1

PROPERTIES: Table 1

COMPOUNDS and SYNONYMS:

allyl alcohol:	[2-propen-1-ol; CAS #107-18-6];
diacetone alcohol:	[4-hydroxy-4-methyl-2-pentanone; CAS #123-42-2];
cyclohexanol:	[hexalin; CAS #108-93-0];
isoamyl alcohol:	[3-methyl-1-butanol; CAS #123-51-3]; and
methyl isobutyl carbinol:	[MIBC; 4-methyl-2-pentanol; CAS #105-30-6].

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L
-MAX: 10 L

SHIPMENT: routine

SAMPLE STABILITY: store in freezer; analyze as soon as possible

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD

BIAS: not significant [1]

OVERALL PRECISION (s_r): see EVALUATION OF METHOD

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 1 mL 5% 2-propanol in CS_2; 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 250 - 300 °C
-COLUMN: 80 - 120 °C

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: glass, 3 m x 2 mm ID, 10% SP-1000 on 80/100 mesh Supelcoport or equivalent

CALIBRATION: solutions of analyte in eluent with internal standard

RANGE AND PRECISION: see EVALUATION OF METHOD

ESTIMATED LOD: 0.01 mg per sample [2]

APPLICABILITY: The working range is 1 to 10 mg/m³ for allyl alcohol and ca. 15 to 150 mg/m³ of the other analytes for a 10-L air sample. This method may be used to determine two or more analytes simultaneously by varying GC conditions (e.g., temperature programming).

INTERFERENCES: High humidity reduces sampling capacity. The methods were validated using a 3 m x 3 mm stainless steel column packed with 10% FFAP on Chromosorb W-AW; other columns with equal or better resolution (e.g., capillary) may be used. Less volatile compounds may displace more volatile compounds on the charcoal.

OTHER METHODS: This method combines and replaces Methods S52, S55, S54, S58 and S60 [3].

REAGENTS:

1. Eluent: Carbon disulfide* (chromatographic) with 5% (v/v) 2-propanol and 0.1% (v/v) hexane, 0.2% (v/v) n-pentadecane or other suitable internal standard.
2. Analyte.
3. Calibration stock solution, allyl alcohol, 0.0128 mg/µL. Dilute 0.128 g allyl alcohol (0.15 mL at 20 °C) to 10 mL with eluent.
4. n-Heptane.
5. DE stock solution, allyl alcohol, 12 mg/mL in n-heptane.
6. Nitrogen, purified.
7. Hydrogen, prepurified.
8. Air, compressed, filtered.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1402-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); all work with it must be done in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 1 to 10 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range (mg analyte per sample): allyl alcohol: 0.02 to 0.1; diacetone alcohol: 0.1 to 5; cyclohexanol: 0.1 to 5; isoamyl alcohol: 0.1 to 5; and MIBC: 0.1 to 2.
   a. Add known amounts of analyte or calibration stock solution to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg analyte).

9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of analyte or DE stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg analyte recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1402-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Methods S52 (allyl alcohol), S55 (diacetone alcohol), S54 (cyclohexanol), S58 (isoamyl alcohol) and S60 (methyl isobutyl carbinol) were issued on January 17, 1975 [3], and validated using 10-L air samples of atmospheres generated in dry air by calibrated syringe drive from the pure substances [1]. Precision and recovery were as shown below, representing non-significant bias in each method:

Method [1,3]	Overall Precision (s_r)	Recovery (%)	Range Studied		Breakthrough @ 2X OSHA	Avg. DE	Measurement Precision (s_r)
			mg/m^3	mg per sample			
S52	0.111	98.8	1.8 to 8.4	0.02 to 0.1	>48 L	0.90	0.023
S55	0.104	91.8	140 to 510	1.1 to 4.7	>48 L	0.78	0.054
S54	0.080	98.9	95 to 380	1 to 4	>48 L	0.99	0.015
S58	0.077	107.6	195 to 680	1.8 to 7	34 L	0.99	0.020
S60	0.080	101.8	45 to 175	0.5 to 2	>48 L	0.99	0.035

REFERENCES:
[1] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] User check, UBTL, NIOSH Sequence #3990-V (unpublished, November 4, 1983).
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 2., U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

METHOD REVISED BY: George Williamson, NIOSH/DPSE; methods originally validated under NIOSH Contract 99-74-45.

Table 1. General information.

Compound	OSHA ACGIH (ppm)	Formula	mg/m³ = 1 ppm @ NTP	M.W.	Density (g/mL)	BP (°C)	VP @ 20 °C, Pa (mm Hg)
Allyl alcohol	2 2 (skin)	$CH_2=CHCH_2OH$; C_3H_6O	2.37	58.08	0.854 @ 20 °C	96-97	2.3 (17)
Diacetone alcohol	50 50	$(CH_3)_2C(OH)CH_2COCH_3$; $C_6H_{12}O_2$	4.75	116.16	0.931 @ 25 °C	167.9	0.1 (0.8)
Cyclohexanol	50 50	$C_6H_{12}O$	4.09	100.16	0.962	161; MP = 24	0.13 (1.0) (5)
Isoamyl alcohol	100 100	$(CH_3)_2CHCH_2CH_2OH$; $C_5H_{12}O$	3.60	88.15	0.813 @ 15 °C	132	0.3 (2)
Methyl isobutyl carbinol	25 25 (skin)	$(CH_3)_2CHCH_2CH(OH)CH_3$; $C_6H_{14}O$	4.18	102.18	0.802	132	0.5 (4)

FORMULA: Table 1

M.W.: Table 1

ALCOHOLS IV

METHOD: 1403
ISSUED: 2/15/84

OSHA/NIOSH/ACGIH: Table 1

PROPERTIES: Table 1

COMPOUNDS (1) 2-Methoxyethanol: [Methyl Cellosolve; CAS #109-86-4];
and (2) 2-Ethoxyethanol: [Cellosolve; CAS #110-80-5]; and
SYNONYMS: (3) 2-Butoxyethanol: [Butyl Cellosolve; CAS #111-76-2].

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.05 L/min

	(1) & (3)	(2)
VOL-MIN:	1 L	1 L
-MAX:	10 L	6 L

SHIPMENT: routine

SAMPLE STABILITY: store in freezer; analyze as soon as possible

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD

BIAS: not significant [1,2]

OVERALL PRECISION (s_r): see EVALUATION OF METHOD

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 1 mL 5% methanol in CH_2Cl_2

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 250 - 300 °C
-COLUMN: (1) 95 °C; (2) 140 °C;
(3) 145 °C

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: glass, 3 m x 2 mm ID, 10% SP-1000 on 80/100 mesh Chromosorb WHP, or equivalent

CALIBRATION: solutions of analyte in eluent with internal standard

RANGE AND PRECISION: see EVALUATION OF METHOD

ESTIMATED LOD: 0.01 to 0.02 mg per sample [3]

APPLICABILITY: This method may be used to determine two or more analytes simultaneously by varying GC conditions (e.g., temperature programming).

INTERFERENCES: High humidity reduces sampling capacity. The methods were validated using a 3 m x 3 mm stainless steel column packed with 10% FFAP on Chromosorb W-AW; other columns with equal or better resolution (e.g., capillary) may be used. Less volatile compounds may displace more volatile compounds on the charcoal.

OTHER METHODS: This method combines and replaces Methods S79 [4], S361 [5], and S76 [4].

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REAGENTS:

1. Eluent: methylene chloride with 5% (v/v) methanol and 0.2% (v/v) 1-heptanol, 0.1% (v/v) ethyl benzene or other suitable internal standard.
2. Analyte.
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, compressed, filtered.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.05L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1403-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10-µL, readable to 0.1 µL.

SPECIAL PRECAUTIONS: None.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.05 L/min for a total sample size of 1 to 10 L (2-methoxyethanol and 2-butoxyethanol) or 1 to 6 L (2-ethoxyethanol).
   NOTE: Maximum flow rate for 2-methoxyethanol and 2-butoxyethanol is 0.2 L/min.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.02 to 8 mg analyte per sample.
   a. Add known amounts of analyte to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of analyte directly onto front sorbent section with a microliter syringe.

c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg analyte recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1403-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Methods S79 (2-methoxyethanol), S361 (2-ethoxyethanol) and S76 (2-butoxyethanol) were issued on February 14, 1975 [4], March 17, 1978 [5], and February 14, 1975 [4], and validated using, respectively, 50-, 6- and 10-L air samples of atmospheres generated by calibrated syringe drive. Precision and recovery were as shown below, representing non-significant bias in each method:

Method	Overall Precision (s_r)	Recovery (%)	Range Studied		Breakthrough @ 2X OSHA	Avg. DE	Measurement Precision (s_r)
			mg/m³	mg per sample			
S79 [1,4]	0.068	93	44 to 160	2 to 8	128 L*	0.98	0.008
S361 [2,5,6]	0.059	107	340 to 1460	2 to 7	>10 L**	1.02	0.009
S76 [1,4]	0.060	92	124 to 490	1 to 5	>44 L*	0.99	0.009

*Dry air.
**90% RH.

REFERENCES:
[1] Documentation of the NIOSH Validation Tests, S76 and S79, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] Backup Data, S361, available as "Ten NIOSH Analytical Methods, Set 6," Order No. PB 288-629 from NTIS, Springfield, VA 22161.
[3] User check, UBTL, NIOSH Sequence #3990-Z (unpublished, November 3, 1983).
[4] NIOSH Manual of Analytical Methods, 2nd ed., V. 2., S76 and S79, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[5] Ibid, V. 5, S361, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[6] NIOSH Research Report, Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Dept. of Health and Human Serices Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY: George Williamson, NIOSH/DPSE; methods originally validated under NIOSH Contracts 99-74-45 and 210-76-0123.

Table 1. General information.

Compound	Exposure Limits (ppm) OSHA	NIOSH	ACGIH	Formula	mg/m³ = 1 ppm @ NTP	M.W.	Density @ 20 °C (g/mL)	BP (°C)	VP @ 20 °C, kPa (mm Hg)
2-Methoxyethanol	25	lowest feasible	25 (skin)	$HOCH_2CH_2OCH_3$; $C_3H_8O_2$	3.11	76.09	0.966	124	0.8 (6)
2-ethoxyethanol	200	lowest feasible	100 (skin)	$HOCH_2CH_2OCH_2CH_3$; $C_4H_{10}O_2$	3.68	90.12	0.931	135	0.5 (4)
2-butoxyethanol	50	—	25 (skin)	$HOCH_2CH_2O(CH_2)_3CH_3$; $C_6H_{14}O_2$	4.83	118.17	0.902	171	0.08 (0.6)

FORMULA: (1) $C_{12}H_8Cl_6$ (Aldrin);
(2) $C_6H_6Cl_6$ (Lindane)
M.W.: (1) 364.93; (2) 290.85

(1) ALDRIN AND (2) LINDANE

METHOD: 5502
ISSUED: 2/15/84

	(1)	(2)
OSHA:	0.5 mg/m³ (skin)	0.25 mg/m³ (skin)
NIOSH:	Group I Pesticides [1]	
ACGIH:	0.5 mg/m³ (skin)	0.25 mg/m³ (skin)

PROPERTIES: (1): solid; MP 104 °C; VP 0.008 Pa (6×10^{-5} mm Hg; 0.12 mg/m³) @ 20 °C
(2): solid; MP 1125 °C; VP 0.0013 Pa (9.4×10^{-6} mm Hg; 0.15 mg/m³) @ 20 °C

SYNONYMS: (1) Aldrin: Octalene; CAS #309-00-2.
(2) Lindane: gamma-hexachlorocyclohexane; CAS #58-89-9.

SAMPLING

SAMPLER: FILTER AND BUBBLER
(glass fiber + 15 mL isooctane)

FLOW RATE: 0.2 to 1 L/min

VOL-MIN: 18 L @ 0.25 mg/m³ of (1) or (2)
-MAX: 240 L

SHIPMENT: transfer bubbler solutions and filters in scintillation vials; pack carefully

SAMPLE STABILITY: at least 1 week @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: (1): 0.15 to 0.5 mg/m³ [2];
(2): 0.3 to 1.7 mg/m³ [2]

BIAS: not significant [2]

OVERALL PRECISION (s_r): (1): 0.092 [2];
(2): 0.086 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ELECTROLYTIC CONDUCTIVITY DETECTOR

ANALYTE: Aldrin, Lindane

FILTER EXTRACTION: isooctane

INJECTION VOLUME: 15 µL

TEMPERATURE-FURNACE: 750 to 770 °C
-TRANSFER: 225 °C
-VENT: 205 to 260 °C
-COLUMN: 160 to 190 °C

GASES-H_2 (furnace): 150 to 160 mL/min
-N_2 (carrier): 140 mL/min

COLUMN: glass, 1.2 m x 3 mm OD; 5% SE-30 on 80/100 mesh acid-washed DMCS Chromosorb W or equivalent

CALIBRATION: solution of analyte in isooctane

RANGE: 5 to 135 µg per sample

ESTIMATED LOD: 3 µg (1) or (2) per sample

PRECISION (s_r): (1): 0.012 [2]; (2) 0.013 [2]

APPLICABILITY: The working range is 0.05 to 1.5 mg/m³ of either pesticide for a 90-L air sample. Evaporation of isooctane from the bubbler necessitates refilling the bubbler frequently.

INTERFERENCES: None identified.

OTHER METHODS: This method combines and replaces S275 [3] and S290 [3]. Lindane has also been sampled with a filter-solid sorbent train [4].

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REAGENTS:

1. Aldrin, reagent grade.*
2. Lindane, reagent grade.*
3. Isooctane, chromatographic grade.
   NOTE: Needed for field use in sample collection.
4. Benzene, reagent grade.*
5. Calibration stock solution, 10 mg/mL. Dissolve 0.1 g accurately weighed Aldrin or Lindane in 1:5 (v:v) benzene:isooctane; dilute to 10 mL. Stable at least one week.
6. Hydrogen, prepurified.
7. Nitrogen, purified.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass fiber filter, organic binder-free (e.g., Gelman Type A/E), 37-mm, held without backup pad in a two-piece polystyrene cassette filter holder connected in series with a midget bubbler containing 15 mL of the collection medium.
   NOTE: a. Do not use filter holders made of Tenite.
   b. Place glass tube, 5 cm x 6 mm ID, plugged with glass wool between the exit cover of the bubbler and the inlet of the personal sampling pump to avoid splashover or solvent condensation.
2. Personal sampling pump, 0.2 to 1 L/min, with flexible connecting tubing.
3. Vial, scintillation, with PTFE-lined cap, graduated at 15 mL.
4. Gas chromatograph with electrolytic conductivity detector, quartz reduction furnace, in-line vent upstream of furnace, integrator and column (page 5502-1).
5. Syringes, 5-, 10- and 25-µL, for making standard solutions and GC injections.
6. Volumetric flasks.
7. Pipets, with pipet bulb.
8. Tweezers.

SPECIAL PRECAUTIONS: Benzene is a suspected human carcinogen; work with it only in a hood.

Aldrin and Lindane are toxic when absorbed through the skin [1].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Add 15 mL isooctane to the bubbler.
3. Sample at 0.5 L/min for 1 to 6 hrs (30 to 180 L).
   NOTE: Check liquid level in the bubbler every 15 min. Maintain between 10 and 15 mL isooctane in the bubbler throughout the sampling period with a volume at the end of sampling of about 10 mL.
4. Remove the bubbler stem and tap it gently against the inside wall of the bubbler to transfer solvent from the stem to the bubbler.
5. Transfer contents of the bubbler to a vial. Rinse the bubbler with 2 mL isooctane. Add the rinse to the vial.
6. Transfer the glass fiber filter to the same vial using tweezers.
7. Cap the vial and pack carefully for shipment.

SAMPLE PREPARATION:

8. Adjust the volume of solution in the vial to 15 mL.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least five solutions covering the range 3 to 135 µg Aldrin or Lindane per sample.
   a. Add calibration stock solution with a microliter syringe to 15 mL isooctane in a vial.
   b. Analyze the working standards together with samples and blanks (steps 10 through 13).
   c. Prepare calibration graph (peak area vs. µg Aldrin or Lindane). Analyze three additional quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.

MEASUREMENT:

10. Set gas chromatograph to manufacturer's specifications and to conditions given on page 5502-1.
11. Mix the contents of the scintillation vial thoroughly.
12. Inject 15 µL sample aliquot using solvent flush technique or autosampler.
    NOTE: Open vent valve for 20 sec, beginning with time of injection, to prevent the solvent peak from entering the furnace.
13. Measure peak area.

CALCULATIONS:

14. Determine the mass, µg, of Aldrin or Lindane found on the sample (filter plus bubbler), W, and average media blank (filter plus bubbler), B, from the measured peak areas and the calibration graph.
15. Calculate the concentration, C (mg/m^3), of Aldrin or Lindane in the air volume sampled, V (L):

$$C = \frac{(W - B)}{V}, \ mg/m^3$$

EVALUATION OF METHOD:

Methods S275 (Aldrin) and S290 (Lindane) were issued on February 27, 1976, and March 26, 1976, respectively [3]. The substances used to generate test atmospheres at 25 °C and 760 mm Hg in dry air were Aldrite emulsifiable concentrate (64% Aldrin) and Ortho-Lindane Borer and Leaf Miner Spray [2]. Collection efficiencies and analytical method recoveries were 1.00 for both substances in the range 22 to 90 µg per sample. Sample filters extracted in isooctane immediately and stored one week at ambient conditions gave recoveries of 103% and 102%, respectively. Overall precision, S_r, was 0.092 for Aldrin and 0.086 for Lindane. No significant bias was found for either substance.

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure During the Manufacture and Formulation of Pesticides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-174 (1978).
[2] Documentation of the NIOSH Validation Tests, S275 and S290, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[3] NIOSH Manual of Analytical Methods, V. 3, S275 and S290, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[4] Hill, R.H. and J.E. Arnold. Arch. Environ. Contam. Toxicol., 8, 621-628 (1979).

METHOD REVISED BY: Gangadhar Choudhary, Ph.D., NIOSH/DPSE; S275 and S290 originally validated under NIOSH Contract CDC-99-74-45.

FORMULA: NaOH, KOH, LiOH, and basic salts

M.W.: 40.00 (NaOH); 56.11 (KOH)

ALKALINE DUSTS

METHOD: 7401
ISSUED: 2/15/84

OSHA: 2 mg/m³ (NaOH)
NIOSH: 2 mg/m³/15 min (NaOH) [1]
ACGIH: C 2 mg/m³ (NaOH)

PROPERTIES: basic, hygroscopic, caustic solids and aerosols; VP not significant

SYNONYMS: alkali; caustic soda; lye; sodium hydroxide (CAS #1310-73-2); potassium hydroxide (CAS #1310-58-3).

SAMPLING

SAMPLER: FILTER
(1-µm PTFE membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 70 L @ 2 mg/m³
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days @ 25 °C [2]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.76 to 3.9 mg/m³ [2]
(360-L samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.062 [2]

MEASUREMENT

TECHNIQUE: ACID-BASE TITRATION

ANALYTE: OH^- (alkalinity)

EXTRACTION: 5.00 mL 0.01 N HCl, 15 min under nitrogen with stirring

TITRATION: 0.01 N NaOH under nitrogen, endpoint by pH electrode

CALIBRATION: 0.01 N NaOH standardized with 0.01 N HCl

RANGE: 0.14 to 1.9 mg per sample [2]

ESTIMATED LOD: 0.03 mg per sample (as NaOH) [2]
(7×10^{-4} mmoles of alkalinity)

PRECISION (s_r): 0.033 [2]

APPLICABILITY: The working range is 0.4 to 5.4 mg/m³ for a 360-L air sample. The method measures total alkalinity due to alkali hydroxides, carbonates, borates, silicates, phosphates, and other basic salts, expressed as equivalents of NaOH.

INTERFERENCES: None identified. Carbon dioxide in the air may react with alkali on the filter to produce carbonates but does not interfere when titrated. The carbonates will produce the equivalent amount of strong alkali that was consumed on the filter [2].

OTHER METHODS: This is Method S381 [3] in a revised format. Method S381 was based, in part, on P&CAM 241 [4].

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REAGENTS:

1. Sodium carbonate, primary standard grade.
2. Hydrochloric acid stock solution, 0.1 N. Standardize with sodium carbonate primary standard.
3. Dilute hydrochloric acid, 0.01 N. Dilute 10.0 mL 0.1 N stock HCl to 100 mL in a volumetric flask with distilled water.
4. Water, distilled, CO_2-free. Boil and cool under N_2 or bubble nitrogen through distilled water for 30 min. Store with an Ascarite trap.
5. Nitrogen, compressed.
6. Sodium hydroxide, 50% w/v.* Dissolve 50 g NaOH in CO_2-free distilled water and dilute to 100 mL.
7. Stock sodium hydroxide, 0.1 N. Dilute 4 mL 50% NaOH to 1.0 L with CO_2-free distilled water. Store under Ascarite trap.
8. Working sodium hydroxide solution, 0.01 N. Dilute 10 mL stock (0.1 N NaOH) to 100 mL with CO_2-free distilled water.
9. Standard buffer solutions, pH 4 and 7.

*See Special Precautions.

EQUIPMENT:

1. Sampler: 37-mm diameter PTFE membrane filter (Millipore Fluoropore or equivalent), 1.0-µm pore size, supported by a cellulose backup pad in a cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. pH meter with pH electrode and recorder.
4. Titration vessel, 150 to 200 mL beaker, flask or jar with cover containing openings for the pH electrode and N_2 inlet and outlet.
5. Stirrer, magnetic, and stir bar.
6. Glass rod, ca. 5-mm diameter and 10 cm long to hold filter under liquid surface in titration vessel.
7. Pipets, 5- and 10-mL.
8. Volumetric flasks, 100- and 1000-mL.
9. Burets, 50-mL, readable to 0.1 mL.

SPECIAL PRECAUTIONS: NaOH solutions are very caustic [1]; handle them with care.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a sample size of 70 to 1000 L. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

3. Transfer the sample filter to a titration vessel with tweezers. Place the filter face down in the titration vessel.
4. Place the end of a glass rod in the center of the filter to maintain the filter below the liquid surface during the analysis.
5. Cover the titration vessel, add 5.00 mL 0.01 N HCl, start the magnetic stirrer and N_2 purge (ca. 100 cm^3/min).
6. Allow to stand 15 min (with stirring).

CALIBRATION AND QUALITY CONTROL:

7. Calibrate the pH meter with pH 4 and 7 buffer solutions.

8. Standardize the 0.1 N HCl stock solution with sodium carbonate in triplicate [4].
   a. Dry 3 to 5 g primary standard grade Na_2CO_3 at 250 °C for 4 hrs. Cool in a dessicator.
   b. Weigh ca. 2.5 g Na_2CO_3 to the nearest mg. Dissolve and make up to exactly 1 L with CO_2-free distilled water. The concentration is ca. 0.05 N Na_2CO_3.
   c. Place 5.00 mL 0.05 N Na_2CO_3 solution into a titration vessel and titrate (potentiometrically) to a pH of 5.
   d. Remove electrodes, rinse them into the titration vessel, and bubble N_2 gas through contents of the titration vessel for 3 to 5 min to remove dissolved CO_2.
   e. Proceed with the titration to the inflection point.
   f. Calculate the normality (N) of the stock HCl solution:

$$N_{HCl} = \frac{(\text{g } Na_2CO_3 \text{ used})(\text{mL } Na_2CO_3 \text{ solution used in titration})}{52.99 \text{ (mL HCl used)}}.$$

9. Standardize the working (ca. 0.01 N) NaOH solution against the standardized HCl solution by following steps 8.c. and 8.e, substituting the standardized HCl stock solution for the Na_2CO_3 solution and the 0.01 N NaOH solution for the 0.1 N HCl solution. Calculate the normality of the NaOH titrating solution.

$$N_{NaOH} = \frac{(N_{HCl})(\text{mL HCl used})}{(\text{mL NaOH used})}.$$

10. Prepare at least two spiked media blank samples to check analytical recoveries at levels expected on the field samples.

MEASUREMENT:

11. Back-titrate the excess HCl in the samples, blanks and spiked blank solutions with the standardized NaOH solution while maintaining the N_2 purge.
12. Record the endpoint for the titration (mL of 0.01 N NaOH used) while observing the pH meter.

CALCULATIONS:

13. Using the volume (mL) of HCl added to the sample (V_{HCl-s}) and average blank (V_{HCl-b}), and the volume of NaOH used for the titration of the sample (V_{NaOH-s}) and average blank (V_{NaOH-b}), the normality of these reagents (N_{HCl} and N_{NaOH}) and the volume of air sampled, V (L), calculate the concentration, C (mg/m³), of alkalinity (as NaOH):

$$C = \frac{\dfrac{(V_{HCl-s})(N_{HCl})}{(V_{NaOH-s})(N_{NaOH})} - \dfrac{(V_{HCl-b})(N_{HCl-b})}{(V_{NaOH-b})(N_{NaOH-b})} \cdot 40{,}000}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S381 [2] was issued on July 8, 1977, and was validated using generated atmosnpheres of NaOH over the range 0.76 to 3.9 mg/m³ using a 360-L sample [2,6]. Overall precision, s_r, was 0.062 with an average recovery of 105%, representing an insignificant bias. The NaOH concentration was independently verified by analyzing additional samples for sodium by atomic absorption spectrophotometry. An overall average collection efficiency of greater than 99% was found by sampling 1 to 360 L in an atmosphere of 7.50 mg/m³ (NaOH) using backup Fluoropore filters and also by sampling (two samples) 615 L using backup impingers filled with water.

REFERENCES:
[1] Criteria for a Recommended Standard...Occupational Exposure to Sodium Hydroxide, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-105 (1975).
[2] Backup Data Report No. S381, Sodium Hydroxide, prepared under NIOSH Contract No. 210-76-0123, available as Order No. PB 275-838 from NTIS, Springfield, VA 22161 (July 8, 1977).
[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, S381, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[4] Ibid, V. 1, P&CAM 241, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[5] Standard Methods for the Examination of Water and Wastewater, 15th Edition, American Public Health Association, American Water Works Association and Water Pollution Control Federation (1981).
[6] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY: R. DeLon Hull, NIOSH/DPSE; S381 originally validated under NIOSH Contract No. 210-76-0123.

FORMULA: $CH_2 = CHCH_2Cl$; C_3H_5Cl

M.W.: 76.53

ALLYL CHLORIDE

METHOD: 1000
ISSUED: 2/15/84

OSHA: 1 ppm
NIOSH: 3 ppm/15 min [1]
ACGIH: 1 ppm; STEL 2 ppm
(1 ppm = 3.13 mg/m³ @ NTP)

PROPERTIES: liquid; d 0.938 g/mL @ 20 °C;
BP 45 °C; MP 135 °C;
VP 39.3 kPa (295 mm Hg; 38.8%) @ 25 °C;
explosive range 3.3 to 11% v/v in air

SYNONYMS: 3-chloro-1-propene; CAS #107-05-1.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 1 L/min

VOL-MIN: 15 L @ 1 ppm
-MAX: 100 L

SHIPMENT: routine

SAMPLE STABILITY: at least 6 weeks @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1.8 to 7.2 mg/m³ [2]
(100-L samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.071 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: allyl chloride

DESORPTION: 1 mL benzene; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 185 to 200 °C
-DETECTOR: 250 °C
-COLUMN: 160 to 200 °C

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: stainless steel, 1.2 m x 6 mm OD;
50/80 mesh Porapak Q or equivalent

CALIBRATION: allyl chloride in benzene

RANGE: 0.05 to 1.5 mg per sample

ESTIMATED LOD: 0.01 mg per sample

PRECISION (s_r): 0.023 [2]

APPLICABILITY: The working range is 0.5 to 10 mg/m³ for a 100-L air sample. The method is applicable to 15-min samples taken at 1 L/min. The upper limit of loading depends on the concentrations of allyl chloride and other substances in the air, including water vapor.

INTERFERENCES: None identified.

OTHER METHODS: This is Method S116 in a revised format [3].

REAGENTS:

1. Benzene, chromatographic quality.*
2. Allyl chloride.
3. Hexane.
4. Calibration stock solution, 7.5 µg/µL. Dilute 75 mg allyl chloride (80.0 µL at 20 °C) to 10 mL with hexane.
5. Nitrogen, purified.
6. Hydrogen, prepurified.
7. Air.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 1000-1).
4. Vials, 2-mL, PTFE-lined caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Volumetric flasks, 10-mL.

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*SPECIAL PRECAUTIONS: Benzene is a suspected human carcinogen. All work should be performed in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 1 L/min for a total sample size of 15 to 100 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL benzene to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.01 to 1.5 mg allyl chloride per sample.
   a. Add known amounts of calibration stock solution to benzene in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg allyl chloride).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.

c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg allyl chloride recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1000-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with benzene, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of allyl chloride found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of allyl chloride in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S116 was issued on May 9, 1975 [3], and validated over the range 1.8 to 7.2 mg/m³ at 25 °C and 759 mm Hg using a 100-L sample [2]. Overall precision, s_r, was 0.071 with average recovery 105.5%, representing a non-significant bias. The concentration of allyl chloride was independently verified by direct gas chromatography. Desorption efficiency was 0.943 in the range 0.15 mg to 0.6 mg allyl chloride per sample. Breakthrough (5% on back section) occurred between 210 and 240 min when sampling an atmosphere containing 7.56 mg/m³ allyl chloride at 0.94 L/min at 0% RH.

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Allyl Chloride, U.S. Department of Health, Education, and Welfare, Education, and Welfare, Publ. (NIOSH) 76-204 (1976).
[2] Documentation of the NIOSH Validation Tests, NIOSH, S116, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 2, S116, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

METHOD REVISED BY: G. David Foley, NIOSH/DPSE; originally validated under NIOSH Contract CDC-99-74-45.

FORMULA: Al

ALUMINUM and compounds, as Al

METHOD: 7013
ISSUED: 2/15/84

M.W.: 26.98 (Al); 101.96 (Al_2O_3)

OSHA: no standard
NIOSH: no standard
ACGIH: 10 mg/m³ (metal, oxide);
5 mg/m³ (pyro powder, welding fume);
2 mg/m³ (soluble salts, alkyls)

PROPERTIES: ductile metal; valence 3; MP 660 °C; VP not significant

SYNONYMS: vary depending upon the compound; Alumina (Al_2O_3); CAS #7429-90-5 (Al); CAS #1344-28-1 (Al_2O_3).

SAMPLING

SAMPLER: FILTER
(0.8-µm cellulose ester membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 10 L @ 5 mg/m³
-MAX: 400 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: none identified

OVERALL PRECISION (s_r): not evaluated

MEASUREMENT

!TECHNIQUE: ATOMIC ABSORPTION, FLAME
!
!ANALYTE: aluminum
!
!ASHING: conc. HNO_3, 6 mL; 140 °C
!
!FINAL SOLUTION: 10% HNO_3, 10 mL
! 1000 µg/mL Cs
!
!FLAME: nitrous oxide-acetylene, reducing
!
!WAVELENGTH: 309.3 nm
!
!BACKGROUND CORRECTION: none used
!
!CALIBRATION: Al^{+++} in 10% HNO_3
!
!RANGE: 50 to 5000 µg per sample [1]
!
!ESTIMATED LOD: 2 µg per sample [4]
!
!PRECISION (s_r): 0.03 [1,4]
!

APPLICABILITY: The working range is 0.5 to 10 mg/m³ for a 100-L sample. This is an elemental analysis, not compound specific. Verify that the types of compounds in the samples are soluble with this ashing procedure. Aliquots of the samples can be analyzed separately for approximately four additional metals.

INTERFERENCES: Cesium at 1000 µg/mL controls ionization in the nitrous oxide-acetylene flame. Iron and HCl at greater than 0.2% (w/w) decrease the sensitivity. Vanadium or H_2SO_4 require 1% (w/w) La as a releasing agent.

OTHER METHODS: This is Method P&CAM 173 for Al [1] in a revised format. Method 7300 (ICP-AES) is an alternate analytical method.

REAGENTS:

1. Nitric acid, conc.
2. Nitric acid, 10% (w/v). Add 100 mL conc. HNO_3 to 500 mL water; dilute to 1 L.
3. Calibration stock solution, 1000 µg Al/mL. Commercially available or dissolve 1.000 g Al wire in minimum volume of (1+1) HCl using small drop of Hg as catalyst. Dilute to 1 L with 1% (v/v) HCl. Filter to remove Hg.
4. Cs solution, 50 mg/mL. Dissolve 73.40 g $CsNO_3$ in 100 mL water; dilute to 1 L.
5. Nitrous oxide.
6. Acetylene.
7. Distilled or deionized water.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-µm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with a nitrous oxide-acetylene burner head and aluminum hollow cathode lamp.
4. Regulators, two-stage, for N_2O and acetylene.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.*
6. Volumetric flasks, 10- and 100-mL.*
7. Micropipets, 5 to 500 µL.*
8. Hotplate, surface temperature 100 and 140 °C.

*Clean with conc. nitric acid and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Perform all acid digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 10 to 400 L. Do not exceed 2 mg total dust loading on the filter.

SAMPLE PREPARATION:

NOTE: The following sample preparation gave quantitative recovery (see EVALUATION OF METHOD). Steps 4 through 9 of Method 7300 or other quantitative ashing techniques may be substituted, especially if several metals are to be determined on a single filter.

3. Open the cassettes and transfer the samples and blanks to clean beakers.
4. Add 6 mL conc. HNO_3 and cover with a watchglass. Start reagent blanks at this point.
5. Heat on hotplate (140 °C) until sample dissolves and a slightly yellow solution is produced. Add acid as needed to completely destroy organic material.
6. When the sample solution is clear, remove watchglass and rinse into the beaker with 10% HNO_3.
7. Place the beakers on a hotplate and allow to go to dryness.
8. When sample is dry, rinse walls of beaker with 3 to 5 mL 10% HNO_3. Reheat for 5 min to dissolve the residue, then allow to air cool.
9. Transfer the solution quantitatively to a 10-mL volumetric flask containing 0.2 mL 50 mg/mL Cs solution. Dilute to volume with 10% HNO_3.
   NOTE: If vanadium or sulfuric acid are present, add 1% (w/w) La as a releasing agent [1,3].

CALIBRATION AND QUALITY CONTROL:

10. Add known amounts, covering the range 0 to 500 µg Al per sample, of calibration stock solution to 100-mL volumetric flasks containing 2.0 mL 50 mg/mL Cs solution and dilute to volume with 10% HNO_3.

11. Analyze the working standards together with the samples and blanks (steps 16 and 17).
12. Prepare a calibration graph of absorbance vs. solution concentration (µg/mL).
13. Aspirate a standard for every 10 samples to check instrument drift.
14. Check recoveries with at least one spiked media blank per 10 samples.
15. Use method of additions occasionally to check for interferences.

MEASUREMENT:

16. Set spectrophotometer according to manufacturer's instructions and to conditions on page 7013-1.
17. Aspirate standards and samples. Record absorbance readings.
    NOTE: If the absorbance values for the samples are above the linear range of the standards, dilute the solutions with 10% HNO_3 and an appropriate amount of the 50 mg/mL Cs solution, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

18. Using the measured absorbances, calculate the corresponding concentrations (µg/mL) of aluminum in the sample, C_s, and average media blank, C_b, from the calibration graph.
19. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration, C (mg/m^3), of aluminum in the volume of air sampled, V (L):

$$C = \frac{(C_s V_s - C_b V_b)}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Estimated LOD was 2 µg Al per sample [4].

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd ed., V. 5, P&CAM 173, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[2] Winefordner, J. D., Ed., Spectrochemical Methods of Analysis, John Wiley & Sons (1971).
[3] Analytical Methods for Atomic Absorption Spectrophotometry, Perkin-Elmer (1976).
[4] User check, UBTL, NIOSH Seq. #3990-0 (unpublished, November 29, 1983).

METHOD WRITTEN BY: Mark Millson and R. DeLon Hull, NIOSH/DPSE.

FORMULA: As

M.W.: 74.92 (As)

ARSENIC and compounds, as As

METHOD: 7900
ISSUED: 2/15/84

OSHA: 0.01 mg/m³
NIOSH: 0.002 mg/m³/15 min [1]
ACGIH: 0.2 mg/m³; suspect carcinogen (As_2O_3)

PROPERTIES: soft, reactive metalloid; MP 848 °C; VP (As_2O_3) 0.0075 Pa (5.6×10^{-8} mm Hg; 0.45 µg As/m³) @ 25 °C; valence ± 3, 5 in salts

SYNONYMS: vary depending upon the compound; CAS #7440-38-2 (As).

SAMPLING

SAMPLER: FILTER (0.8-µm cellulose ester membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 30 L @ 0.002 mg/m³
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: stable if refrigerated

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: see APPLICABILITY

OVERALL PRECISION (s_r): not evaluated

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, FLAME ARSINE GENERATION

ANALYTE: arsenic

ASHING: conc. HNO_3, 3 mL; conc. H_2SO_4, 1 mL; conc. $HClO_4$, 1 mL; 140 °C

FINAL SOLUTION: 4% H_2SO_4, 25 mL

FLAME: hydrogen-argon

WAVELENGTH: 193.7 nm

BACKGROUND CORRECTION: D_2 or H_2 continuum

CALIBRATION: As in 4% H_2SO_4

RANGE: 0.05 to 2.0 µg per sample [2]

ESTIMATED LOD: 0.02 µg per sample [2]

PRECISION (s_r): 0.11 [2]

APPLICABILITY: The working range is 0.00025 to 0.01 mg/m³ for a 200-L air sample and 0.002 to 0.07 mg/m³ for a 30-L air sample. This method collects particulate arsenic only; if arsenic trioxide vapor is present, use the sampler in Method 7901. This is an elemental analysis, not compound specific. Volatile organic arsenic compounds, As_2O_3 vapor, and arsine are not collected efficiently by this sampling method.

INTERFERENCES: Background absorption is overcome by the use of D_2 or H_2 continuum.

OTHER METHODS: This method is a revision of P&CAM 139 [2]; a similar method appears in the criteria document [1]. Method 7901 uses a sampler designed to collect As_2O_3 vapor and an alternate measurement technique (graphite furnace-AAS). Method 7300 (ICP-AES) also gives an alternate measurement technique.

REAGENTS:

1. Nitric acid, conc.
2. Hydrochloric acid, conc.
3. Sulfuric acid, conc.
4. Perchloric acid, conc.*
5. Calibration stock solution, 1000 µg/mL.* Commercially available or dissolve 1.320 g primary standard As_2O_3 in 25 mL 20% (w/v) KOH. Neutralize with 20% (v/v) HNO_3 to a phenolphthalein endpoint. Add 10 mL conc. HNO_3 and dilute to 1 L with distilled or deionized water.
6. Ashing acid, 3 volumes HNO_3, 1 volume H_2SO_4, and 1 volume $HClO_4$.
7. Hydrogen.
8. Argon.
9. Distilled or deionized water.
10. Sodium borohydride, pellets.
11. Air, compressed.

*See Special Precautions.

EQUIPMENT:

1. Sampler: cellulose ester filter, 0.8-µm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with a three-slot burner head or quartz tube furnace, and arsenic hollow cathode lamp or EDL and arsine generation system.
4. Regulators, two-stage, for air, hydrogen and argon.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.*
6. Volumetric flasks, 25- and 100-mL.*
7. Pipets, volumetric, as needed.*
8. Hotplate, surface temperature 140 °C.

*Clean all glassware with conc. nitric acid before use and rinse thoroughly with distilled or deionized water.

SPECIAL PRECAUTIONS: Arsenic is a recognized carcinogen; handle appropriately [1]. Perform all perchloric acid digestions in a perchloric acid fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative filter in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 30 to 1000 L. Do not exceed 2 mg total dust loading on the filter.

SAMPLE PREPARATION:

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
   NOTE: Analyze the backup pad separately if qualitative indication of As_2O_3 vapor is desired. Use Method 7901 if quantitative collection of As_2O_3 vapor is desired.
4. Add 5 mL ashing acid and cover with a watchglass.
5. Heat on hotplate (140 °C) until the solution is colorless.
6. Add 1 mL conc. HNO_3 and/or 70% $HClO_4$ drop by drop as needed to complete the ashing.
7. Remove the watchglass.
8. Heat on 140 °C hotplate until dense SO_3 fumes appear.
9. Allow the mixture to cool.
10. Transfer the solution quantitatively to a 25-mL volumetric flask.
11. Dilute to volume with distilled or deionized water.

CALIBRATION AND QUALITY CONTROL:

12. Add known amounts, covering the range 0.2 to 8 µg As/100 µL (0.05 to 2 µg As per sample), of 1000 µg/mL As calibration stock solution to 100-mL volumetric flasks containing 4 mL conc. H_2SO_4 and dilute to volume with distilled or deionized water.
13. Analyze the working standards together with the blanks and samples (steps 18 through 25).
14. Prepare a calibration graph of absorbance vs. solution concentration (µg/mL).
15. Analyze a standard for every 10 samples.
16. Check analytical recoveries with at least one spiked media blank per 10 samples.
17. Use method of additions occasionally to check for interferences.

MEASUREMENT:

18. Set spectrophotometer according to manufacturer's recommendations and to conditions on page 7900-1.
19. Set up arsine generator as per manufacturer's instructions.
20. Pipet 5 mL aliquot of the 25-mL sample into the arsine generation flask.
21. Add 25 mL distilled or deionized water, 3 mL conc. HCl, and mix well.
22. Connect the flask to the generation system.
23. Introduce a single sodium borohydride pellet or sodium borohydride solution to the sample solution.
24. Allow the gases to flush into the flame of the atomic absorption instrument.
25. Record the absorbance readings.

    NOTE: If the absorbance values of the samples are above the linear range of the standards, dilute the solutions, or use a smaller aliquot, reanalyze, and use the appropriate dilution factor in calculations.

CALCULATIONS:

26. Using the measured absorbances, calculate the corresponding solution concentrations (µg/mL) of As in the sample, C_s, and average media blank, C_b, from the calibration graph.
27. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration, C (mg/m^3), of As in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

This method was evaluated in July, 1976, over the range 0.02 to 3 µg per sample by lab testing with spiked filters. Precision and accuracy data are given on page 7900-1 [2].

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Inorganic Arsenic, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 75-149 (175).

[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 139, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).

METHOD REVISED BY: Mark Millson, NIOSH/DPSE.

FORMULA: As_2O_3

ARSENIC TRIOXIDE, as As

METHOD: 7901
M.W.: 197.84
ISSUED: 2/15/84

OSHA: 0.01 mg/m³ (As)
NIOSH: 0.002 mg/m³ (As)/15 min [1]
ACGIH: suspect carcinogen

PROPERTIES: solid; MP 275 °C or 313 °C(sublimes); VP 0.0075 Pa (5.6 x 10^{-8} mm Hg; 0.45 µg As/m³) @ 25 °C

SYNONYMS: arsenous acid anhydride; arsenous sesquioxide; arsenolite; claudetite; CAS #1327-53-3

SAMPLING

SAMPLER: FILTER (Na_2CO_3-impregnated, 0.8-µm cellulose ester membrane + backup pad)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 30 L @ 0.01 mg/m³
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.67 to 32 µg/m³ [2,3] (400-L samples)
BIAS: not significant [2,3]

OVERALL PRECISION (s_r): 0.075 [2,3]

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, GRAPHITE FURNACE

ANALYTE: arsenic

ASHING: 15 mL HNO_3 + 6 mL H_2O_2; 150 °C

FINAL SOLUTION: 10 mL 1% HNO_3, 0.1% Ni^{++}

WAVELENGTH: 193.7 nm; D_2 or H_2 correction

GRAPHITE TUBE: non-pyrolytic

INJECTION: 25 µL; DRY: 100 °C, 70 sec;
CHAR: 1300 °C, 30 sec;
ATOMIZE: 2700 °C, 10 sec

CALIBRATION: As in 1% HNO_3, 0.1% Ni^{++}

RANGE: 0.3 to 13 µg per sample

ESTIMATED LOD: 0.06 µg per sample

PRECISION (s_r): 0.029 [4,5]

APPLICABILITY: The working range is 0.001 to 0.06 mg/m³ for a 200-L air sample. This method collects particulate arsenic compounds as well as arsenic trioxide vapor. If only total particulate arsenic is of interest, the use of the treated filter and analysis of the backup pad is not required. Arsine is not collected by this sampling method.

INTERFERENCES: Background absorption is overcome by the use of a deuterium background corrector. Matrix modification with Ni^{++} solution allows the use of a higher char temperature in the graphite furnace. Other particulate arsenic compounds will interfere.

OTHER METHODS: This method combines and replaces P&CAM 346 [4], S309 [5], and P&CAM 286 [9]. Method 7300 (ICP-AES) and arsine generation (Method 7900 and the criteria document method [1]) are for particulate arsenic compounds. Other methods (P&CAM 173 [8], P&CAM 180 [6], and P&CAM 188 [7]) have not been revised because of interferences or poor sensitivity.

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REAGENTS:

1. Nitric acid, conc.
2. Nitric acid, 1% (w/v). Dilute 10 mL conc. HNO_3 to 1 L with distilled or deionized water.
3. Hydrogen peroxide, 30% (w/w).
4. Ni^{++} in 1% HNO_3, 1000 µg/mL. Dilute 4.95 g $Ni(NO_3)_2$ to 1 L with 1% HNO_3.
5. Calibration stock solution*, 1000 µg As/mL, commercially available, or dissolve 1.320 g primary standard As_2O_3 in 25 mL 20% (w/v) KOH. Neutralize with 20% (v/v) HNO_3 to a phenolphthalein endpoint. Dilute to 1 L with 1% HNO_3.
6. 1 M Na_2CO_3:glycerol solution, 20:1. Dissolve 9.5 g sodium carbonate in 100 mL distilled or deionized water. Add 5 mL pure glycerol.
7. Distilled or deionized water.
8. Argon.

*See Special Precautions.

EQUIPMENT:

1. Sampler: Cellulose ester membrane filter, 0.8-µm pore size, 37-mm diameter, and cellulose backup pad in cassette filter holder treated as follows:
   a. Remove inlet plug from the loaded cassette.
   b. Add 250 µL 20:1 Na_2CO_3:glycerol solution with a micropipet directly onto filter (wet entire surface).
   c. Attach to vacuum source and draw 30 to 60 L clean air through the filter.
   d. Let dry overnight. Replace the inlet plug.
   e. Use within one week.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
   NOTE: The treated filter has a high pressure drop; a personal sampling pump with flow rate control is required.
3. Atomic absorption spectrophotometer with graphite furnace atomizer arsenic electrodeless discharge lamp and background correction.
4. Regulator, two-stage for argon.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL with watchglass covers.*
6. Volumetric flasks, 10-mL.*
7. Assorted volumetric pipets as needed.*
8. Hotplate, surface temperature to 150 °C.
9. Steambath.

*Clean all glassware with conc. nitric acid and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Arsenic is a carcinogen [1]; handle appropriately. Perform all digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 30 to 1000 L. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

3. Transfer both the treated filter and backup pad to a clean beaker.
4. Add 15 mL conc. HNO_3 and cover with a watchglass.
   NOTE: Start reagent blanks at this step.
5. Heat on a 150 °C hotplate until the liquid volume is reduced to about 1 mL.
6. Carefully rinse the material on the bottom of the watchglass, and the sides of the beaker into the sample solution with distilled water. Add 6 mL 30% H_2O_2.

7. Evaporate just to dryness on the steambath.
8. Cool beakers. Add 10.0 mL 1000 µg/mL Ni^{++} solution, cover, and mix for 30 min in an ultrasonic bath.

CALIBRATION AND QUALITY CONTROL:

9. Dilute the calibration stock solution 1:100 with 1000 µg/mL Ni^{++} solution. This standard is 10.0 µg/mL As. Prepare fresh daily.
10. Prepare working standards covering the range 0 to 1.25 µg/mL As.
    a. Add aliquots of the 10.0 µg/mL As solution to 10-mL volumetric flasks and dilute to volume with 1000 µg/mL Ni^{++} solution.
    b. Analyze the working standards together with the sampler and blanks (steps 13 and 14).
    c. Prepare calibration graph (absorbance vs. solution concentration, µg/mL). Inject a standard for every other sample to check instrument drift.
11. Check recoveries with at least two spiked media blanks per ten samples.
12. Use method of additions occasionally to check for interferences.

MEASUREMENT:

13. Set spectrophotometer according to manufacturer's recommendations to conditions on page 7901-1.
14. Inject standards and samples. Record absorbance (peak height) readings.
    NOTE: If the absorbance values for the samples are above the linear range of the standards, dilute the solutions with the 1000 µg/mL Ni^{++} solution, reanalyze, and use the appropriate dilution factor in calculations.

CALCULATIONS:

15. Record the actual solution volumes to which the sample, V_s (mL), and media blanks, V_b (mL) were diluted in step 8.
16. Calculate the solution concentration of arsenic in the sample, C_s (µg/mL), and average media blank, C_b (µg/mL), from the calibration graph.
17. Calculate the concentration of arsenic, C (mg/m^3), in the air volume sampled, V(L):

$$C = \frac{(C_s V_s - C_b V_b)}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method S309 [5] was issued on September 26, 1975, and validated with aerosols generated from As_2O_3 solutions in dilute NaOH [3]. Method P&CAM 346 was developed in August, 1981, over the range 0.67 to 32.2 $\mu g/m^3$ for a 400-L air sample, corresponding to 0.268 to 12.8 µg As per sample [2]. Atmospheres were generated by passing air over heated As_2O_3. Collection efficiencies (CE) for As_2O_3 under these conditions were determined to be 0.42 and 0.67 for untreated 0.8-µm cellulose ester membrane filters, and cellulose backup pads, respectively. Under the same conditions, the Na_2CO_3-treated filter had CE = 0.93 [9]. This method was used in a lead-acid battery manufacturing plant in which vapor was found to be significant [10].

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Inorganic Arsenic, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 75-149 (1975).
[2] Carlin, L. M., G. Colovos, D. Garland, M. E. Jamin, M. Klenck, T. J. Long, and C. L. Nealy. Analytical Methods Evaluation and Validation - As, Ni, W, V, Talc, and Wood Dust, Rockwell International, Final Report on NIOSH Contract No. 210-79-0060; available as Order No. PB 83-155325 from NTIS, Springfield, VA 22161.

[3] Documentation of the NIOSH Validation Tests, S309, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[4] NIOSH Manual of Analytical Methods, 2nd ed., V. 7, P&CAM 346, U.S. Department of Health and Human Services, Publ. (NIOSH) 82-100 (1982).
[5] Ibid, V. 3, S309, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[6] Ibid, V. 1, P&CAM 180, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[7] Ibid, P&CAM 188.
[8] Ibid, V. 5, P&CAM 173, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141-C (1979).
[9] Ibid, P&CAM 286.
[10] Costello, R. J., P. M. Eller, and R. D. Hull. Measurement of Multiple Inorganic Arsenic Species, Am. Ind. Hyg. Assoc. J., 44, 21-28 (1983).

METHOD REVISED BY: Mark Millson and P. M. Eller, Ph.D., CIH, NIOSH/DPSE; P&CAM 346 originally developed under NIOSH Contract 210-79-0060.

FORMULA: $(C_6H_5CO)_2O_2$; $C_{14}H_{10}O_2$

BENZOYL PEROXIDE

METHOD: 5009
ISSUED: 2/15/84

M.W.: 242.22

OSHA: 5 mg/m³
NIOSH: 5 mg/m³ [1]
ACGIH: 5 mg/m³

PROPERTIES: solid; MP 103 °C; d 1.334 g/mL @ 25 °C; VP not significant [1]; autoignition temperature 8 °C

SYNONYMS: dibenzoyl peroxide, benzoyl superoxide, CAS# 94-36-0.

SAMPLING

SAMPLER: FILTER
(0.8-µm cellulose ester membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 40 L @ 5 mg/m³
-MAX: 400 L

SHIPMENT: refrigerated

SAMPLE STABILITY: 9% loss from filter after 1 week @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 3 to 19 mg/m³ [2]
(90-L samples)

BIAS: none identified [2]

OVERALL PRECISION (s_r): 0.060 [2]

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: benzoyl peroxide

EXTRACTION: ethyl ether, 10 mL

INJECTION VOLUME: 20 µL

PRESSURE-COLUMN: 9000 kPa (1300 psi)

MOBILE PHASE: 70/30 methanol/water; 1.6 mL/min

DETECTOR: UV photometer @ 254 nm

COLUMN: 250 mm x 3 mm ID stainless steel; Spherisorb ODS (spherical silica particles with 5% bonded coating of octadecyl groups) or equivalent

CALIBRATION: benzoyl peroxide in ethyl ether

RANGE: 0.2 to 1.7 mg per sample [2]

ESTIMATED LOD: 0.01 mg per sample [4]

PRECISION (s_r): 0.024 [2]

APPLICABILITY: The working range is 1 to 8.5 mg/m³ for a 200-L air sample.

INTERFERENCES: None identified.

OTHER METHODS: This is Method S253 [3] in a revised format. A non-specific gravimetric method appears in the criteria document [1].

REAGENTS:

1. Benzoyl peroxide, 99% pure.*
2. Ethyl ether, purified, without stabilizer.
3. Methanol, distilled in glass.
4. Water, deionized and distilled.
5. Calibration stock solution, 10 mg/mL. Dissolve 250 mg benzoyl peroxide in ethyl ether and dilute to 25 mL. Stable at least one week at 4 °C.

*See Special Precautions.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-µm pore size, 37-mm diameter, with backup pad in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Vials, 20-mL, PTFE-lined caps.
4. High performance liquid chromatograph, 254-nm UV detector, sample injection valve with a 20-µL external sample loop, syringe filter, integrator and column (page 5009-1).
5. Tweezers.
6. Microliter syringes, 10- and 100-µL.
7. Volumetric flasks, 10- and 25-mL, assorted sizes.
8. Pipet, 10-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Benzoyl peroxide is a flammable solid and may explode when heated; it will attack some plastics, rubber, and coatings [1].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 40 to 400 L. Do not exceed 2 mg particulate loading on the filter.
3. Ship samples in an insulated container with bagged refrigerant.

SAMPLE PREPARATION:

4. Immediately upon receipt at laboratory, refrigerate the samples.
5. As soon as possible after receipt, transfer each filter to a clean vial with tweezers.
6. Pipet 10 mL ethyl ether into each vial; screw on cap. Swirl to mix.

CALIBRATION AND QUALITY CONTROL:

7. Calibrate daily with at least five working standards covering the range 0.01 to 1.7 mg per sample.
   a. Add calibration stock solution with a microliter syringe to ethyl ether in a 10-mL volumetric flask and dilute to the mark.
   b. Analyze together with samples, blanks and control samples (steps 10 through 12).
   c. Prepare calibration graph of peak area vs. mass (mg) of benzoyl peroxide per sample.
8. Determine recovery of benzoyl peroxide from filters at least once for each lot of samplers in the calibration range (step 7). Prepare three filters at each of five levels plus media blanks.
   a. Add aliquot of calibration stock solution with a microliter syringe directly to a media blank filter in a vial.
   b. Prepare and analyze together with working standards (steps 5, 6 and 10 through 12).
   c. Prepare a graph of recovery vs. mg benzoyl peroxide recovered.
9. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and recovery graph are in control.

MEASUREMENT:

10. Set high pressure liquid chromatograph according to manufacturer's recommendations and to conditions given on page 5009-1.
11. Flush sample loop thoroughly with sample (0.1 mL) and inject sample.
12. Measure peak area.

CALCULATIONS:

13. Read mass, mg (corrected for recovery), of benzoyl peroxide found on sample filters, W (mg), and on average blank filters, B (mg), from calibration graph.
14. Calculate concentration, C (mg/m^3), of benzoyl peroxide in the air volume sampled, V (L):

$$C = \frac{(W - B) \cdot 10^3}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method S253 was issued on January 21, 1977 [3], and validated over the range 3.1 to 19.1 mg/m^3 at 26 °C and 764 mm Hg, using 90-L samples [2,5]. The collection efficiency of the filter was determined to be 1.00 since no benzoyl peroxide was detected on a backup filter mounted directly behind the front filter. Storage stability studies on the filter held in the filter cassette indicated a 9.3% decrease in the amount of benzoyl peroxide recovered from the filter after one week. Benzoyl peroxide was stable in ethyl ether at room temperature for at least one week. Overall precision, s_r, was 0.060. The data from these experiments were not adequate for determining the bias. Recovery was 0.97 in the range 0.225 to 0.900 mg per sample for 18 spiked samples.

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Benzoyl Peroxide, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-166 (1977).
[2] NIOSH Backup Data Report, S253, for Benzoyl Peroxide, prepared under NIOSH Contract No. 210-76-0123, available as "Ten NIOSH Analytical Methods, Set 2," Order No. PB 271-464, from NTIS, Springfield, VA 22161.
[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, S253, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[4] UBTL Memorandum, UBTL Analytical Laboratory Report for Benzoyl Peroxide, Sequence #2182-J.
[5] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY: Julie R. Okenfuss, NIOSH/DPSE; S253 originally validated under NIOSH Contract 210-76-0123.

FORMULA: Be

M.W.: 9.01

BERYLLIUM and compounds, as Be

METHOD: 7102
ISSUED: 2/15/84

OSHA: 2 µg/m³; C 5 µg/m³
NIOSH: 2 µg/m³; 25 µg/m³/30 min [1]
ACGIH: 2 µg/m³ (suspect carcinogen)

PROPERTIES: hard, light metal; valence +2;
MP 1284 to 1300 °C;
d 1.85 g/mL (20 °C)

SYNONYMS: CAS #7440-41-7; other synonyms vary as to compound.

SAMPLING

SAMPLER: FILTER
(0.8-µm cellulose ester membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 25 L @ 2 µg/m³
-MAX: 1000 L @ 2 µg/m³

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 2.7 to 11.8 µg/m³ [2]
(40-L samples)

BIAS: not significant

OVERALL PRECISION (s_r): 0.064 [2]

MEASUREMENT

!
!TECHNIQUE: ATOMIC ABSORPTION, GRAPHITE FURNACE
!
!ANALYTE: beryllium
!
!ASHING REAGENTS: HNO_3, 10 mL; H_2SO_4, 1 mL
!
!CONDITIONS: 150 °C until brown fumes disappear;
! 400 °C to dense fumes of H_2SO_4
!
!FINAL SOLUTION: 2% Na_2SO_4, 3% H_2SO_4;
! 10 mL
!
!GRAPHITE FURNACE: 110 °C dry 20 sec;
! 900 °C char 10 sec;
! 2800 °C atomize 18 sec
!
!WAVELENGTH: 234.9 nm
!
!BACKGROUND CORRECTION: D_2 or H_2 arc
!
!INJECTION VOLUME: 10 µL
!
!CALIBRATION: Be^{++} in 2% Na_2SO_4,
! 3% H_2SO_4
!
!RANGE: 0.05 to 1 µg per sample [3]
!
!ESTIMATED LOD: 0.005 µg per sample [3]
!
!PRECISION (s_r): 0.008 [3]
!

APPLICABILITY: The working range is 0.5 to 10 µg/m³ for a 90-L air sample. The method is applicable to ceiling measurements using a 25-L air sample.

INTERFERENCES: Calcium interference is masked by 3% (v/v) sulfuric acid. Sodium, potassium, and aluminum enhance beryllium absorbance. This effect is overcome by addition of 2% (w/v) sodium sulfate to both standards and samples. Perchloric, phosphoric, and hydrofluoric acids produce interferring non-atomic peaks. These must be removed by digesting to dryness.

OTHER METHODS: This is Method P&CAM 288 [3], which replaced Method S339 [4], in a revised format. Flame atomic absorption and plasma emission (ICP-AES) are not sensitive enough for beryllium at these levels.

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REAGENTS:

1. Nitric acid, conc.
2. Sulfuric acid, conc.
3. Sodium sulfate, reagent grade.
4. Sodium sulfate, 2% (w/v)/3% sulfuric acid (v/v). Add 10 g sodium sulfate and 15 mL H_2SO_4 to deionized water. Dilute to 500 mL.
5. Calibration stock solution, 1000 µg Be/mL,* commercially available; or dissolve 1.000 g Be metal in a minimum volume of 1+1 HCl, dilute to 1 L with 1% (v/v) HCl.
6. Argon, prepurified.
7. Water, distilled or deionized.

*See Special Precautions.

EQUIPMENT:

1. Sampler: mixed cellulose ester membrane filter, 0.8-µm pore size, 37-mm diameter in three-piece cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with graphite furnace and background corrector.
4. Beryllium hollow cathode lamp.
5. Pressure regulator, two-stage, for Argon.
6. Beakers, Phillips, 125-mL.*
7. Watchglasses.*
8. Volumetric flasks, 10-mL.*
9. Pipets, 10-mL delivery, with pipet bulb.*
10. Automatic pipettor with tips, 10-µL and assorted sizes for standards.
11. Hotplate, 150 to 400 °C.
12. Waterbath, 60 to 70 °C.
13. Bottles, polyethylene, 25-mL.

*Clean all glassware with conc. nitric acid and rinse thoroughly before use.

SPECIAL PRECAUTIONS: Beryllium is very toxic and a suspected human carcinogen [1]. Perform all acid digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative filter in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a sample size of 25 to 1000 L. Do not exceed 2 mg total dust loading on the filter.

SAMPLE PREPARATION:

3. Open cassettes and transfer filters to clean Phillips beakers.
4. Add 10 mL conc. HNO_3 and 1 mL conc. H_2SO_4. Cover with watchglass.
5. Heat in fume hood on hotplate (150 °C) until brown fumes of HNO_3 disappear, then at 400 °C until dense fumes of H_2SO_4 appear.
   NOTE: Verify that the compounds in the samples are soluble with this ashing procedure, e.g., ore or mining samples will require HF in the digestion. If additional ashing acids are used (e.g., HF, $HClO_4$, or H_3PO_4), evaporate to complete dryness at this point.
6. Cool and rinse watchglass and sides of beaker with distilled water and evaporate just to dryness. Remove beaker immediately and air-cool.
7. Pipet 10.0 mL 2% Na_2SO_4/3% H_2SO_4 solution into beaker and cover.
8. Heat in 60 to 70 °C waterbath for 10 min. Allow to stand overnight before analysis to ensure complete dissolution of $BeSO_4$.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least five working standards over the range 0.005 to 1 µg Be per sample.

a. Add known amounts of calibration stock solution to 2% Na_2SO_4/3% H_2SO_4 in 10-mL volumetric flasks and dilute to the mark. Store in polyethylene bottles. Stable at least four weeks.
b. Analyze together with samples and blanks (steps 11 and 12).
NOTE: Analyze working standards alternately with the samples to compensate for the increasing Be signal as the graphite tube ages.

10. Analyze three quality control blind spikes and three analyst spikes.

MEASUREMENT:

11. Set spectrophotometer and graphite furnace according to manufacturer's recommendations and to conditions on page 7102-1.
12. Inject 10-µL aliquots of samples into graphite tube. Record absorbance (peak height mode).

CALCULATIONS:

13. Read absorbance of samples, A; average media blanks, A_b; reagent blanks, A_r; and working standards, A_s.
14. Using the working standard, C_s (µg/mL), analyzed adjacent to the sample of interest, calculate concentration, C (µg/m³), of Be in the air volume sampled, V (L):

$$C = \frac{[A - (A_b - A_r)] \cdot C_s \cdot 10^4}{A_s V}, \mu g/m^3$$

EVALUATION OF METHOD:

This method was evaluated using NBS Standard Reference Material No. 2675 for Be over the range of 0.1 to 0.4 µg Be/filter (equivalent to one-half to two times the OSHA PEL). Beryllium recovery was 98.2% with a measurement precision, s_r, of 0.008 [3]. This method is an improvement of S339 [4], which was validated over the range of 2.68 to 11.84 µg/m³ using a 40-L sample. Mean recovery was 106.9% with overall precision of 0.064 [2].

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Beryllium, U.S. Department of Health, Education and Welfare, Publ. (NIOSH) 72-10268 (1972); and as revised in August, 1977 in NIOSH testimony at OSHA hearing.
[2] Documentation of the NIOSH Validation Tests, S339, U.S. Department of Health, Education and Welfare, Publ. (NIOSH) 77-185 (1977).
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 5, P&CAM 288, U.S. Department of Health, Education and Welfare, Publ. (NIOSH) 79-141 (1979).
[4] Ibid., V. 3, S339, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

METHOD REVISED BY: Mary Ellen Cassinelli, NIOSH/DPSE; S339 validated under NIOSH Contract CDC-99-74-45.

(1) BROMOXYNIL and (2) BROMOXYNIL OCTANOATE

FORMULA: (1) $C_7H_3Br_2NO$
(2) $C_{15}H_{17}Br_2NO_2$

METHOD: 5010
ISSUED: 2/15/84

M.W.: (1) 276.93; (2) 403.13

OSHA: no standard
NIOSH: no standard
ACGIH: no standard

PROPERTIES: (1) liquid; BP 194 to 195 °C;
(2) solid; MP 45 to 47 °C

SYNONYMS: (1): 2,6-dibromo-4-cyanophenol; 3,5-dibromo-4-hydroxybenzonitrile; CAS# 1689-84-5.
(2): 2,6-dibromo-4-cyanophenyl octanoate; CAS #1689-99-2.

SAMPLING

SAMPLER: FILTER
(2-µm PTFE membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 90 L
-MAX: 400 L

SHIPMENT: refrigerated; protect from light

SAMPLE STABILITY: at least 14 days @ 4 °C in the dark [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: none identified

OVERALL PRECISION (s_r): not evaluated

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: Bromoxynil; Bromoxynil octanoate

EXTRACTION: 3 mL acetonitrile; 60 min

COLUMN: µ-Bondapack C_{18}, 25 cm x 4.6 mm ID reverse phase or equivalent

MOBILE PHASE: acetonitrile/water gradient; 1 mL/min

DETECTION: UV detector @ 254 nm

CALIBRATION: solutions of analytes in acetonitrile

RANGE: 1.5 to 30 µg per sample [1]

ESTIMATED LOD: (1) 0.6 and (2) 0.3 µg per sample [1]

PRECISION (s_r): (1) 0.011 @ 18 µg per sample [1]
(2) 0.042 @ 35 µg per sample [1]

APPLICABILITY: The working range is 0.01 to 0.2 mg/m³ for a 150-L air sample. This method permits the simultaneous analysis of both analytes.

INTERFERENCES: None known. Both analytes photodecompose.

OTHER METHODS: A gas chromatographic method has been described [2].

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REAGENTS:

1. Bromoxynil.
2. Bromoxynil octanoate.
3. Acetonitrile, HPLC grade.
4. Water, distilled, deionized.
5. Calibration stock solution, 1 mg/mL. Dissolve 0.100 g each of Bromoxynil and Bromoxynil octanoate in acetonitrile; dilute to 100 mL in a volumetric flask. Prepare daily, in duplicate.

EQUIPMENT:

1. Sampler: PTFE-coated glass fiber (Pallflex T60A20) or 2-µm PTFE membrane (GHIA), 37-mm diameter.
   NOTE: Use opaque or light-protected cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Jars, ointment, 60-mL, squat form, with PTFE-lined screw caps.
4. Volumetric flasks, 10 and 100-mL.
5. Pipet, 3-mL.
6. Vials (for autosampler).
7. Liquid chromatograph with gradient capability, UV detector (254 nm) and column, µ-Bondapak C_{18} (Waters Assoc., Milford, MA), 250 mm x 4.6 mm reverse phase.

SPECIAL PRECAUTIONS: None.

SAMPLING:

1. Calibrate each personal sampling pump to 1.5 L/min with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 90 to 400 L. Do not exceed 2 mg total dust loading on filter.
3. After sampling, cap the filter holders, ship at 4 °C and protect from light.

SAMPLE PREPARATION:

4. Transfer the filter to a jar. Add 3.0 mL acetonitrile and desorb with occasional swirling for at least 1 hr.
5. Filter an aliquot through a 0.5-µm PTFE filter using a syringe with a Swinnex adaptor to remove particulate. Transfer the aliquot to a sample vial and seal.

CALIBRATION AND QUALITY CONTROL:

6. Calibrate daily with at least five working standards over the range 0.6 to 30 mg of both analytes per sample.
   a. Add known amounts of calibration stock solution to acetonitrile in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg analyte).
      NOTE: Before processing any samples, demonstrate, through the analysis of a solvent blank, that all glassware and reagents are interference-free. Each time a new set of samples is analyzed or there is a change in reagents, process a solvent blank as a safeguard against chronic laboratory contamination.

MEASUREMENT:

7. Set the liquid chromatograph to the conditions on page 5010-1 using the following mobile phase gradient: 50% CH_3CN/50% H_2O for 10 min; 10 min gradient to 100% CH_3N; hold 10 min; 2 min gradient to 50% CH_3CN/50% H_2O; hold 15 min.

8. Inject 100 µL sample extract with a high-pressure syringe or a sampling loop. Record the volume injected to the nearest 0.5 µL. Under these conditions, the retention times are 3.6 min for Bromoxynil and 33 min for Bromoxynil octanoate.
9. Measure peak area.
   NOTE: If the peak area exceeds the linear range of the system, dilute with acetonitrile and reanalyze. If the peak area measurement is hindered by the presence of interferences, other chromatographic conditions may be required.

CALCULATIONS:

10. Read the mass of analytes (including appropriate aliquot factors) in the sample extract, W (µg), and average media blank, B (µg), from the calibration graph.
11. Determine the concentrations, C (mg/m^3), of each analyte in the air volume sampled, V (L):

$$C = \frac{W - B}{V}.$$

EVALUATION OF METHOD:

This method was developed with laboratory samples during the period June to September, 1983 [1]. PTFE-coated glass fiber filters were spiked with 50 µg Bromoxynil and 90 µg Bromoxynil octanoate, after which 90 L of clean air at 80% RH was drawn through the filters. Recoveries averaged 93% for Bromoxynil and 100% for Bromoxynil octanoate with relative standard deviations, s_r, of 0.046 and 0.020, respectively. Storage at ambient conditions for 14 days gave recoveries of 70 to 80% for both compounds, while storage under refrigeration for 25 days or at ambient conditions for two days followed by refrigeration for 23 days gave recoveries in the range 95 to 98%.

REFERENCES:

[1] Arthur D. Little, Inc., Backup Data Report prepared under NIOSH Contract 200-82-2528 (unpublished, October 7, 1983).
[2] Thrun, K., J. Harris, and V. Grady. "Sampling and Analysis Procedures for Pesticide Manufacturing Wastes," Report, EPA Contract No. 68-02-3111 (1982).

METHOD WRITTEN BY: K. T. Menzies, K. J. Beltis, A. C. Roche, Arthur D. Little, Inc.; and B. R. Belinky, NIOSH/DPSE.

FORMULA: $CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3$; C_4H_8O

M.W.: 72.11

2-BUTANONE

METHOD: 2500
ISSUED: 2/15/84

OSHA: 200 ppm
NIOSH: 200 ppm [1]
ACGIH: 200 ppm; STEL 300 ppm
(1 ppm = 2.95 mg/m³ @ NTP)

PROPERTIES: liquid; d 0.805 g/mL @ 20 °C;
BP 79.6 °C; MP -86 °C;
VP 13 kPa (100 mm Hg; 13% v/v) @ 25 °C;
explosive range 2 to 10% v/v in air

SYNONYMS: methyl ethyl ketone; MEK; CAS #78-93-3.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(Ambersorb XE-347, 160 mg/80 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L
-MAX: 12 L

SHIPMENT: routine

SAMPLE STABILITY: 6 weeks @ 25 °C [2]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 295 to 1180 mg/m³ [2]

BIAS: - 8.0% [2]

OVERALL PRECISION (s_r): 0.069 [2]

MEASUREMENT

!
!TECHNIQUE: GAS CHROMATOGRAPHY, FID
!
!ANALYTE: 2-butanone
!
!DESORPTION: 1 mL CS_2; stand 30 min
!
!INJECTION VOLUME: 5 µL
!
!TEMPERATURE-INJECTION: 250 °C
! -DETECTOR: 300 °C
! -COLUMN: 55 to 75 °C
!
!GASES-CARRIER: N_2 or He, 25 mL/min
!
!COLUMN: glass or stainless steel, 4 m x 2 mm ID;
! 20% SP-2100/0.1% Carbowax 1500 on
! Supelcoport 100/120
!
!CALIBRATION: 2-butanone solutions in CS_2
!
!RANGE: 0.15 to 5 mg per sample
!
!ESTIMATED LOD: 0.004 mg per sample [2,3]
!
!PRECISION (s_r): 0.04 [2]
!

APPLICABILITY: The working range is 50 to 1500 mg/m³ (17 to 508 ppm) for a 3-L sample. The method is applicable to 15-min samples. This method was developed to give improved sample stability compared to conventional charcoal tubes and should be used if more than 3 days will elapse between sampling and analysis. Side-by-side comparisons of this method and Method S3 were made in a sporting goods manufacturing plant in which MIBK, THF, and toluene were also present.

INTERFERENCES: Under these conditions, acetone and isopropanol have retention times similar to 2-butanone. Mass spectrometry and other GC columns, e.g., SP-1000, or 30 m x 0.32 mm WCOT capillary coated with 1 µm DB-1, are aids to resolving interferences.

OTHER METHODS: This method, originally designated P&CAM 365 [2], is similar, except for the sampler, to Methods P&CAM 127 [4] and S3 [5,6], which it replaces.

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REAGENTS:

1. Eluent: Carbon disulfide*, chromatographic quality, containing 0.1% (v/v) benzene* or other suitable internal standard.
2. 2-Butanone.
3. Nitrogen, purified.
4. Hydrogen prepurified.
5. Air, filtered.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID. Two sections of 60/80 mesh Ambersorb XE-347 separated by 2-mm foam plug (front = 160 mg, back = 80 mg) (SKC Cat. No. 226-62-347, or equivalent).
2. Personal sampling pump, 0.02 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 2500-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10-µL, readable to 0.1 µL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); work with it only in a hood.

Benzene is a human carcinogen.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 1 to 12 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.004 to 5 mg 2-butanone per sample.
   a. Add known amounts of 2-butanone to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg 2-butanone).
9. Determine desorption efficiency (DE) at least once for each batch of Ambersorb XE-347 used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of 2-butanone directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg 2-butanone recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2500-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of 2-butanone found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of 2-butanone in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Lab testing with spiked samplers and atmospheres generated by syringe pump/air dilution; verified by infrared absorption. Breakthrough (80% RH, 200 ppm, 0.3 L/min) = 16.4 L; DE (4 to 18 mg per sample) = 1.03; storage stability (0.7 to 4 mg per sample) = 90% after six weeks at 25 °C; precision and accuracy as given on page 2500-1 (15 samples) [2]. A user check gave an estimated LOD of 0.004 mg 2-butanone per sample [3].

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Ketones, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-173 (1978).
[2] Slick, E. J., NIOSH, unpublished data (1983).
[3] User check, UBTL, NIOSH Seq. #3990-J (unpublished, August 29, 1983).
[4] NIOSH Manual of Analytical Methods, V. 1, P&CAM 127, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[5] Ibid., V. 2, S3, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[6] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).

METHOD WRITTEN BY: Edward J. Slick; Judd Posner, Ph.D.; and David Smith, CIH; NIOSH/DPSE.

FORMULA: Cd

M.W.: 112.40 (Cd); 128.40 (CdO)

CADMIUM and compounds, as Cd

METHOD: 7048
ISSUED: 2/15/84

OSHA: 0.1, C 0.3 (fume);
0.2, C 0.6 (dust)
NIOSH: 0.04; 0.2/15 min [1]
ACGIH: 0.05 (dust, salts);
C 0.05 (fume)
(all units mg/m³)

PROPERTIES: soft metal; valence 2; BP 765 °C;
MP 320.9 °C

SYNONYMS: vary depending upon the compound; CAS #7440-43-9 (Cd); CAS #1306-19-0 (CdO).

SAMPLING

SAMPLER: FILTER
(0.8-µm cellulose ester membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 25 L @ 0.1 mg/m³
-MAX: 1500 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.12 to 0.98 mg/m³ [2]
(25-L samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.06 [2]

MEASUREMENT

!
!TECHNIQUE: ATOMIC ABSORPTION, FLAME
!
!ANALYTE: cadmium
!
!ASHING: conc. HNO_3, 6 mL; 140 °C
! conc. HCl, 6 mL; 400 °C
!
!FINAL SOLUTION: 0.5 N HCl; 25 mL
!
!FLAME: air-acetylene, oxidizing
!
!WAVELENGTH: 228.8 nm
!
!BACKGROUND CORRECTION: D_2 or H_2 lamp
!
!CALIBRATION: Cd in 0.5 N HCl
!
!RANGE: 2.5 to 30 µg per sample [3]
!
!ESTIMATED LOD: 0.05 µg per sample [6]
!
!PRECISION (s_r): 0.03 [2,3,6]
!
!

APPLICABILITY: The working range is 0.1 to 2 mg/m³ for a 25-L sample, and 0.01 to 0.2 mg/m³ for a 250-L sample. This is an elemental analysis and it will not distinguish Cd fume from Cd dust. Aliquots of the samples can be analyzed separately for many additional metals.

INTERFERENCES: Background correction is required to control molecular or flame absorption. Iron does not interfere at 20 parts Fe to 1 part Cd [2,4].

OTHER METHODS: This method combines and replaces P&CAM 173 [3], S312 [4], and S313 [5]. A similar method appears in the criteria document [1]. Method 7300 (ICP-AES) is an alternate analytical method.

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REAGENTS:

1. Nitric acid, conc.
2. Hydrochloric acid, conc.
3. Hydrochloric acid, 0.5 N. Add 41.5 mL conc. HCl to water; dilute to 1 L.
4. Calibration stock solution, 100 µg Cd/mL.* Commercially available or dissolve 0.100 g Cd metal in minimum volume of (1+1) HCl. Dilute to 1 L with 0.5 N HCl.
5. Distilled-deionized water.
6. Air, filtered.
7. Acetylene.

*See Special Precautions.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-µm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with an air-acetylene burner head and cadmium hollow cathode lamp.
4. Regulators, 2-stage, for air and acetylene.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.*
6. Volumetric flasks, 25- and 100-mL.*
7. Micropipets, 5 to 300 µL.*
8. Hotplate, surface temperature 400 °C.

*Clean with conc. nitric acid and rinse thoroughly before use.

SPECIAL PRECAUTIONS: Perform all acid digestions in a fume hood.

Cadmium compounds are very toxic [1]; handle with extra care.

SAMPLING:

1. Calibrate each personal sampling pump with a representative filter in line.
2. Sample at an accurately known flow rate between 2 and 3 L/min for 15 min (30 to 45 L) for ceiling measurements, or at 1 to 3 L/min for a total sample size of 25 to 1500 L for TWA measurements. Do not exceed a filter loading of approximately 2 mg total dust.

SAMPLE PREPARATION:

NOTE: The following sample preparation gave quantitative recovery (see EVALUATION OF METHOD) [2,3,5]. Steps 4 through 9 of Method 7300 or other quantitative ashing techniques may be substituted, especially if several metals are to be determined on a single filter.

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
4. Add 2 mL conc. HNO_3, cover with a watchglass, and heat on hotplate (140 °C) until the volume is reduced to ca. 0.5 mL. Start reagent blanks at this point.
5. Repeat 2 more times using 2 mL conc. HNO_3 each time.
6. Add 2 mL conc. HCl, cover with a watchglass, and heat on hotplate (400 °C) until the volume is reduced to ca. 0.5 mL.
7. Repeat 2 more times using 2 mL conc. HCl. Do not allow the solution to go to dryness at any point.
8. Cool solution and add 10 mL distilled water.
9. Transfer the solution quantitatively to a 25-mL volumetric flask.
10. Dilute to volume with distilled water.

CALIBRATION AND QUALITY CONTROL:

11. Add known amounts, covering the range 0 to 30 µg Cd per sample, of calibration stock solution to 100-mL volumetric flasks and dilute to volume with 0.5 N HCl.

12. Analyze the working standards together with the blanks and samples (steps 17 and 18).
13. Prepare a calibration graph of absorbance vs. solution concentration (µg/mL).
14. Aspirate a standard for every 10 samples to check instrument drift.
15. Check recoveries with at least 2 spiked media blanks per 10 samples.
16. Use method of additions occasionally to check for interferences.

MEASUREMENT:

17. Set spectrophotometer according to manufacturer's recommendations and to conditions on page 7048-1.
18. Aspirate standards and samples. Record absorbance readings.
    NOTE: If the absorbance values for the samples are above the linear range of the standards, dilute the solutions with 0.5 N HCl, reanalyze, and use the appropriate dilution factor in calculations.

CALCULATIONS:

19. Using the measured absorbances, calculate the corresponding concentrations (µg/mL) of cadmium in the sample, C_s, and average media blank, C_b, from the calibration graph.
20. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration, C (mg/m^3), of cadmium in the volume of air sampled, V (L):

$$C = \frac{(C_s V_s - C_b V_b)}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method S312 was issued on June 12, 1976 [4], and validated over the range 0.12 to 0.98 mg/m^3 for a 25-L sample of CdO dust [2,4]. Method S313 was issued on November 26, 1976 [5], and validated over the range 0.12 to 0.57 mg/m^3 for a 25-L sample of Cd fume, and over the range 0.04 to 0.18 mg/m^3 for a 140-L sample of Cd fume [2,3]. The estimated LOD is 0.05 µg Cd per sample [6].

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Cadmium, Appendix II, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-192 (1976).
[2] Documentation of the NIOSH Validation Tests, S312 and S313, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 5, P&CAM 173, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[4] Ibid, V. 3, Method S312, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[5] Ibid, Method S313.
[6] User check, UBTL, NIOSH Seq. #3990-M (unpublished, November 29, 1983).

METHOD REVISED BY: Mark Millson and R. DeLon Hull, NIOSH/DPSE; S312 and S313 originally validated under NIOSH Contract CDC-94-74-45.

FORMULA: Ca

M.W.: 40.08 (Ca); 56.08 (CaO)

CALCIUM and compounds, as Ca

METHOD: 7020
ISSUED: 2/15/84

OSHA: 5 mg/m³ (CaO)
ACGIH: 2 mg/m³ (CaO),
5 mg/m³ ($Ca(OH)_2$);
10 mg/m³ ($CaCO_3$, $CaSiO_3$)

PROPERTIES: soft, reactive metal; valence 2;
MP 848 °C; VP not significant

SYNONYMS: Quicklime (CaO); limestone ($CaCO_3$); marble ($CaCO_3$); hydrated lime ($Ca(OH)_2$);
CAS #1305-78-8 (CaO); CAS #1305-62-0 ($Ca(OH)_2$); CAS #1317-65-3 ($CaCO_3$).

SAMPLING

SAMPLER: FILTER
(0.8-µm cellulose ester membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 20 L @ 5 mg/m³
-MAX: 400 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 2.6 to 10.2 mg/m³ [3]
(85-L samples)

BIAS: not significant [3]

OVERALL PRECISION (s_r): 0.063 [3]

MEASUREMENT

!
!TECHNIQUE: ATOMIC ABSORPTION, FLAME
!
!ANALYTE: calcium
!
!ASHING: conc. HNO_3, 6 mL; 140 °C
! 60% $HClO_4$, 2 mL; 400 °C
!
!FINAL SOLUTION: 5% HCl, 100 mL
! 1000 µg/mL Cs; 1000 µg/mL La
!
!FLAME: air-acetylene, reducing
!
!WAVELENGTH: 422.7 nm
!
!BACKGROUND CORRECTION: none used
!
!CALIBRATION: Ca^{++} in 5% HCl
!
!RANGE: 0.08 to 1.7 mg per sample [2]
!
!ESTIMATED LOD: 0.001 mg per sample [5]
!
!PRECISION (s_r): 0.02 [3,5]
!

APPLICABILITY: The working range is 1 to 20 mg/m³ for an 85-L sample. This is an elemental analysis, not compound specific. Verify that the compounds in the samples are soluble with the ashing procedure. Aliquots of the samples can be analyzed separately for many additional metals.

INTERFERENCES: The use of 1000 µg/mL Cs controls ionization in the flame caused by metals such as Na, K, Li, and Mg. The presence of Si, Al and H_3PO_4 require the use of 1% (w/w) La as a releasing agent.

OTHER METHODS: This method combines and replaces P&CAM 173 [1] and S205 [2]. Method 7300 (ICP-AES) is an alternate analytical method.

(3)

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REAGENTS:

1. Nitric acid, conc.
2. Hydrochloric acid, conc.
3. Hydrochloric acid, 5% (v/v). Add 50 mL conc. HCl to 500 mL water; dilute to 1 L.
4. Calibration stock solution, 1000 µg Ca/mL. Commercially available or add 50 mL deionized water and minimum volume of HCl (20 mL) to dissolve 2.498 g $CaCO_3$. Dilute to 1 L with deionized water.
5. Cs solution, 50 mg/mL. Dissolve 73.40 g $CsNO_3$ in water to make 1 L solution.
6. La solution, 50 mg/mL. Dissolve 156 g $La(NO_3)_3 \cdot 6H_2O$ in water to make 1 L solution.
7. Distilled or deionized water.
8. Air, filtered.
9. Acetylene.
10. Perchloric acid, 60% w/v.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-µm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with an air-acetylene burner head and calcium hollow cathode lamp.
4. Regulators, 2-stage, for air and acetylene.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.*
6. Volumetric flasks, 25- and 100-mL.*
7. Micropipets, 5 to 500 µL.*
8. Hotplate, surface temperature 140 and 400 °C.

*Clean with conc. HNO_3 and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Perform all perchloric acid digestions in a perchloric acid fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 20 to 400 L. Do not exceed 2 mg total dust loading on the filter.

SAMPLE PREPARATION:

NOTE: The following sample preparation gave quantitative recovery (see EVALUATION OF METHOD). Steps 4 through 9 of Method 7300 or other quantitative ashing techniques may be substituted, especially if several metals are to be determined on a single filter.

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
4. Add 5 mL conc. HNO_3 and cover with a watchglass. Start reagent blanks at this point.
5. Heat on hotplate (140 °C) until most of the acid has evaporated.
6. Add 2 mL conc. HNO_3 and 1 mL 60% $HClO_4$.
7. Heat on 400 °C hotplate until dense fumes of perchloric acid appear.
8. Remove watchglass and rinse into the beaker with distilled water.
9. Place the beakers on the 400 °C hotplate and allow to go to dryness.
10. Cool each beaker and dissolve the residues in 5 mL 5% HCl.
11. Transfer the solution quantitatively to a 100-mL volumetric flask containing 2 mL of 50 mg/mL Cs solution and 2 mL of 50 mg/mL La solution.
    NOTE: Dilute to a smaller volume (e.g., 10 mL) with proportionally less Cs and La if required for sensitivity of analysis for other metals in the sample.
12. Dilute to volume with 5% HCl.

CALIBRATION AND QUALITY CONTROL:

13. Add known amounts, covering the range 0 to 500 µg Ca per sample, of calibration stock solution to 100-mL volumetric flasks containing 2 mL each of the 50 mg/mL Cs and La solutions and dilute to volume with 5% HCl.
14. Analyze the working standards along with the samples and blanks (steps 19 and 20).
15. Prepare a calibration graph of absorbance vs. solution concentration (µg/mL).
16. Aspirate a standard for every 10 samples to check instrument drift.
17. Check recoveries with at least one spiked media blank per 10 samples.
18. Use method of additions occasionally to check for interferences.

MEASUREMENT:

19. Set spectrophotometer according to manufacturer's recommendations and to conditions on page 7020-1.
20. Aspirate standards and samples. Record absorbance readings.
    NOTE: If the absorbance values for the samples are above the linear range of the standards, dilute the solutions with 5% HCl and an appropriate amount of the 50 mg/mL Cs and La solutions, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

21. Using the measured absorbances, calculate the corresponding concentrations (µg/mL) of calcium in the sample, C_s, and average media blank, C_b, from the calibration graph.
22. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration, C (mg/m^3), of calcium in the volume of air sampled, V (L):

$$C = \frac{(C_s V_s - C_b V_b)}{V}, \ mg/m^3.$$

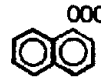
EVALUATION OF METHOD:

Method S205 [2] was issued on September 26, 1975, and validated over the range 2.6 to 10.2 mg/m^3 using an 85-L sample by lab testing with spiked filters and generated atmospheres of CaO, verified by EDTA titration [3]. Collection efficiency of 1.00 was determined for the sampling device. Precision and accuracy data are given on page 7020-1. An additional check showed an estimated LOD of 1 µg Ca per sample [5].

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 5, P&CAM 173, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[2] Ibid, V. 3, S205, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1979).
[3] Documentation of the NIOSH Validation Tests, S205, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[4] Analytical Methods for Atomic Absorption Spectrophotometry, Perkin-Elmer (1976).
[5] User check, UBTL, NIOSH Seq. #3990-Q (unpublished, November 29, 1983).

METHOD REVISED BY: Mark Millson and R. DeLon Hull, NIOSH/DPSE; S205 originally validated under NIOSH Contract CDC-99-74-45.

FORMULA:  ; $C_{12}H_{11}NO_2$

CARBARYL

METHOD: 5006
ISSUED: 2/15/84

M.W.: 201.22

OSHA: 5 mg/m³
NIOSH: 5 mg/m³,
Group II Pesticide [1,2]
ACGIH: 5 mg/m³; STEL 10 mg/m³

PROPERTIES: solid, crystal; d 1.230 g/mL @ 20 °C;
BP decomposes; MP 142 °C;
VP 0.7 Pa (0.005 mm Hg; 50 mg/m³)
@ 20 °C

SYNONYMS: Sevin, 1-naphthalenol methylcarbamate, CAS# 63-25-2.

SAMPLING

SAMPLER: FILTER
(glass fiber)

FLOW RATE: 1 to 2 L/min

VOL-MIN: 2 L
-MAX: 720 L

SHIPMENT: ship filters in 25-mL
scintillation vials

SAMPLE STABILITY: at least 7 days @ 25 °C [2]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 2 to 13 mg/m³ [3]
(90-L samples)

BIAS: not significant [3]

OVERALL PRECISION (s_r): 0.057 [3]

MEASUREMENT

TECHNIQUE: VISIBLE ABSORPTION SPECTROPHOTOMETRY

ANALYTE: p-nitrobenzenediazonium fluoroborate
complex

SAMPLE WORKUP: 20 mL 0.1 M methanolic potassium
hydroxide; to 2-mL aliquot, add
17 mL glacial acetic acid; add
1 mL p-nitrobenzenediazonium
fluorobate

WAVELENGTH: 475 nm

CALIBRATION: Carbaryl in methylene chloride

RANGE: 0.01 to 1.6 mg per sample [4]

ESTIMATED LOD: not determined

PRECISION (s_r): 0.015 [3]

APPLICABILITY: The working range is 0.1 to 16 mg/m³ for a 100-L air sample. The method has sufficient sensitivity to measure STEL exposures as low as 0.4 mg/m³.

INTERFERENCES: Phenols such as 1-naphthol will give a positive interference [4]. Interferences from other aromatic carbamates and phenoxyacetic acid pesticides may occur but have not been documented.

OTHER METHODS: This is Method S273 in a revised format [4].

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REAGENTS:

1. Carbaryl, reagent grade.*
2. Methanol, absolute.*
3. Methylene chloride, distilled in glass.*
4. 0.1 M KOH in absolute methanol. Dissolve 0.1 mole (5.612 g) in 10 mL of methanol in a 1-L volumetric flask; dilute to mark with methanol.
5. Glacial acetic acid.*
6. p-Nitrobenzenediazonium fluoroborate. Dissolve 25 mg in 5 mL methanol. Add 20 mL glacial acetic acid. Prepare fresh daily.
7. Calibration stock solution, 2 mg/mL. Dissolve an accurately weighed 20 mg Carbaryl in methylene chloride to make 10 mL solution.

*See Special Precautions.

EQUIPMENT:

1. Sampler: 37-mm filter cassette with 37-mm Type A glass fiber filter.
2. Personal sampling pump, 1 to 2 L/min, with flexible connecting tubing.
3. Spectrophotometer capable of measuring at 475 nm with matched glass cuvettes (1 cm path length).
4. Vials, scintillation, 25-mL, with PTFE-lined screw caps.
5. Tweezers.
6. Syringe, Luer-Lok glass, 10-mL, with 13-mm stainless steel filter holder and PTFE filters.
7. Shaker, mechanical wrist-action.
8. Flasks, volumetric, 10-mL and 1 L.
9. Pipets, 1-, 2-, 17- and 20-mL with pipet bulb.
10. Syringes or micropipets, 10-, 25- and 50-µL.

SPECIAL PRECAUTIONS: Carbaryl is a cholinesterase inhibitor; use precautions to prevent skin contamination [1,2].

Methylene chloride is toxic; use only in a hood. Methanol is flammable and toxic (flash point = 11 °C); use only in a hood. Glacial acetic acid is corrosive; handle only with gloves and facial splash protection.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 2 L/min for a sample size of 2 to 720 L.
3. Within 1 hr after sampling, remove the filter carefully to prevent to sample loss and place it in the vial. Handle filter only with tweezers.

SAMPLE PREPARATION:

4. Add 20 mL 0.1 M methanolic KOH to the vial containing the filter.
5. Place the vial on a shaker for 5 min.
6. Transfer 2 mL sample solution to another vial.
7. Add 17 mL glacial acetic acid and cover vial with a PTFE-lined screw-cap. Mix by swirling.
8. Add 1 mL p-nitrobenzenediazonium fluoroborate solution. Allow the color to develop for 20 min.
9. Use a syringe fitted with a PTFE filter, to eliminate glass fibers, to transfer the solution from the sample vial to the cuvette .

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least five working standards over the range 0.01 to 1.6 mg Carbaryl per sample.
    a. Add known amounts of calibration stock solution to 20 mL 0.1 M methanolic KOH in vials.
    b. After 5 min, transfer 2.0 mL of each solution into a clean vial.
    c. Prepare as in steps 7 through 9.
    d. Analyze together with samples and blanks (steps 12 through 14).
    e. Prepare calibration graph (absorbance vs. mg Carbaryl).
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

12. Set spectrophotometer at 475 nm.
13. Adjust baseline to zero with distilled water in both cells.
14. Read the absorbance of the sample against the absorbance of the blank.

CALCULATIONS:

15. Determine the mass, mg, of Carbaryl found on the filter, W, and average media blank, B, from the calibration graph.
16. Calculate the concentration, C (mg/m^3), of Carbaryl in the air volume sampled, V (L):

$$C = \frac{(W - B) \cdot 10^3}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method S273 [4] was issued on February 27, 1976, and validated over the range of 1.96 to 13.4 mg/m^3 at 24 °C and 763 mm Hg [3]. Overall precision, s_r, was 0.057 with an average recovery of 102%, representing a non-significant bias. The concentration of Carbaryl was independently verified by a Thermo Systems particle mass monitor. Generated atmospheres were produced by nebulization of a toluene solution of a commercial formulation of Sevin containing 15% by weight Carbaryl. No Carbaryl was detected in bubblers (containing 0.1 M KOH in methanol) placed behind the glass fiber filters when 90-L air samples were taken of an atmosphere containing 15 mg/m^3 Carbaryl. Thus, it was concluded that Carbaryl vapor was not a significant factor.

REFERENCES:

[1] NIOSH Criteria for a Recommended Standard...Occupational Exposure During the Manufacture and Formulation of Pesticides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-174 (July, 1978).
[2] NIOSH Criteria for a Recommended Standard...Occupational Exposure to Carbaryl, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-107 (1976).
[3] Documentation of NIOSH Validation Tests, S273, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[4] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3, S273, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[5] Official Methods of Analysis of the Association of Official Analytical Chemists, 11th ed., Assoc. of Official Analytical Chemists (1970).

METHOD REVISED BY: P. Fey O'Connor, NIOSH/DPSE; S273 originally validated under NIOSH Contract 99-74-45.

FORMULA: C

M.W.: 12.01

CARBON BLACK

METHOD: 5000
ISSUED: 2/15/84

OSHA: 3.5 mg/m³
NIOSH: 3.5 mg/m³ (or PAH 0.1 mg/m³) [1]
ACGIH: 3.5 mg/m³; STEL 7 mg/m³

PROPERTIES: solid; sublimes @ 3650 °C; may contain polynuclear aromatic hydrocarbons [1]

SYNONYMS: acetylene black, amorphous carbon, furnace black, lamp black; CAS #1333-86-4.

SAMPLING

SAMPLER: FILTER
(tared 5-µm PVC membrane)

FLOW RATE: 1.5 to 2 L/min

VOL-MIN: 85 L @ 3.5 mg/m³
-MAX: 570 L @ 3.5 mg/m³

SHIPMENT: routine

SAMPLE STABILITY: indefinitely

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 2 to 8 mg/m³
(100-L samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.056 [2]

MEASUREMENT

TECHNIQUE: GRAVIMETRIC (FILTER WEIGHT)

ANALYTE: airborne particulate material

BALANCE: 0.01 mg sensitivity or better; use same balance before and after sample collection

CALIBRATION: National Bureau of Standards Class M weights

RANGE: 0.3 to 2 mg per sample

ESTIMATED LOD: 0.2 mg per sample

PRECISION: 0.08 mg per sample [5]

APPLICABILITY: The working range is 1.5 to 10 mg/m³ for a 200-L air sample. This method is not applicable for the determination of "cyclohexane-solubles" [1]. This analysis is simple but the method is nonspecific. Information on any other particulate materials present should be assessed. The method may be extended to higher air concentrations (e.g., nuisance dust levels) by collecting a smaller sample volume [4].

INTERFERENCES: The presence of any other particulate material in the air being sampled will be a positive interference since this is a gravimetric method.

OTHER METHODS: This is Method S262 [3] in a revised format. It is similar, except for collecting device, to the method described in the carbon black criteria document [1].

Preceding page blank

REAGENTS:

1. Drierite or other suitable desiccant.

EQUIPMENT:

1. Sampler: 37-mm, 5-μm pore size PVC filter and stainless steel support screen in 37-mm, cassette filter holder.
2. Personal sampling pump, 1.5 to 2 L/min, with flexible connecting tubing.
3. Microbalance capable of weighing to 0.01 mg.
4. Desiccator.
5. Petri dish, plastic, or other filter holder for weighing.

SPECIAL PRECAUTIONS: Carbon black containing polynuclear aromatic hydrocarbons (cyclohexane extractable materials) in excess of 0.1% (w/w) should be treated as a suspect carcinogen [1].

PREPARATION OF FILTERS BEFORE SAMPLING:

1. Dry the filters to constant weight in a desiccator. This takes about 12 hrs.
2. Equilibrate the filters to the balance room conditions for at least 1 hr.
3. Weigh the filter and record the tare weight, W_1 (mg). Zero the balance before each filter weighing.
4. Assemble the sampler.

SAMPLING:

5. Calibrate each personal sampling pump with a representative sampler in line.
6. Sample at 1.5 to 2 L/min. Do not exceed a filter loading of approximately 2 mg total dust.

SAMPLE PREPARATION:

7. Wipe dust from the external surface of the filter cassette with a moist paper towel to minimize contamination. Discard the paper towel.
8. Transfer the filter to an open Petri dish and dry to constant weight in a desiccator (about 12 hrs). Equilibrate the filter to the balance room conditions for at least 1 hr.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate the balance with National Bureau of Standards Class M weights.
10. Use the same balance for weighing filters before and after sample collection.
11. Zero the balance before each weight reading.

MEASUREMENT:

12. Weigh the filters, including field blanks, and record the post-sampling weight, W_2 (mg).

CALCULATIONS:

13. Calculate the concentration, C (mg/m^3), of carbon black in the air volume sampled, V (L):

$$C = \frac{(W_2 - W_1) + B}{V} \cdot 10^3, \ mg/m^3$$

where: W_1 = tare weight of equilibrated filter before sampling (mg)
W_2 = post-sampling weight of equilibrated filter after sampling (mg)
B = mean change in field blank filter weights between tare and post-sampling (mg) (+ or -).

EVALUATION OF METHOD:

Method S262 [3] was issued on January 30, 1976, and validated over the range 1.9 to 7.7 mg/m^3 for a 200-L sample and over the range 7.8 to 28 mg/m^3 for a 100-L sample using Vulcan XC72 (0.03-µm particle size; Cabot Corp.) in a Wright Dust Feeder [2]. Overall precision, S_r, was 0.056. Collection efficiency was between 99 and 100%.

REFERENCES

[1] NIOSH Criteria for a Recommended Standard ... Occupational Exposure to Carbon Black, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-204, 80-88 (1978).

[2] Documentation of the NIOSH Validation Tests, S262 and S349, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).

[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 3, S262, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

[4] Ibid, S349, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

[5] Unpublished data from Non-textile Cotton Study, NIOSH/DRDS/EIB.

METHOD REVISED BY: Kathy Morring and Frank Hearl, P.E., NIOSH/DRDS; S262 and S349 originally validated under NIOSH Contract CDC-99-74-45.

FORMULA: S=C=S; CS_2

M.W.: 76.14

CARBON DISULFIDE

METHOD: 1600
ISSUED: 2/15/84

OSHA: 20 ppm; C 30 ppm; P 100 ppm
NIOSH: 1 ppm; 10 ppm/15 min [1]
ACGIH: 10 ppm (skin)
(1 ppm = 3.11 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.263 g/mL @ 20 °C;
BP 46.5 °C; MP -112 °C;
VP 40 kPa (300 mm Hg; 40% v/v) @ 20 °C;
explosive range 1 to 50% v/v in air

SYNONYMS: dithiocarbonic anhydride; CAS #75-15-0.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg, and sodium sulfate, 270 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 3 L @ 10 ppm
-MAX: 25 L

SHIPMENT: dryer attached to charcoal

SAMPLE STABILITY: 1 week @ 25 °C;
6 weeks @ 0 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 46 to 183 mg/m³ [2]
(6-L samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.059 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, SULFUR FPD

ANALYTE: sulfur

DESORPTION: 10 mL benzene; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 150 °C
-DETECTOR: 145 °C
-COLUMN: 30 °C

CARRIER GAS: N_2 or He, 20 mL/min

COLUMN: glass, 2 m x 6 mm OD, 5% OV-17 on 80/100 mesh GasChrom Q or equivalent

CALIBRATION: CS_2 in benzene solution

RANGE: 0.1 to 0.5 mg per sample

ESTIMATED LOD: 0.02 mg per sample [6]

PRECISION (s_r): 0.052 [2]

APPLICABILITY: The working range is 17 to 167 mg/m³ (5 to 54 ppm) for a 6-L air sample and is applicable to ceiling determinations. Better sensitivity may be obtained by using less desorbing solvent or higher sampling flow rates if high humidity is not present [1,5]. This method has been used extensively in the viscose rayon industry and at carbon disulfide production facilities.

INTERFERENCES: No interference occurs from hydrogen sulfide [5]. Water vapor is a potential sampling interferent [5] which is removed by the drying tube. Alternate GC columns, e.g., 5% OV-210 on Chromosorb G-HP, are aids to resolution of analytical interferences.

OTHER METHODS: This is Method S248 in a revised format [4]. The criteria document method [1,5] uses a higher flow rate. This method replaces P&CAM 179 which uses a similar collection method but extraction-atomic absorption for analysis [3].

Preceding page blank

REAGENTS:

1. Carbon disulfide, chromatographic quality.*
2. Benzene, reagent grade.*
3. Calibration stock solution, 0.5 mg/µL. Dilute 0.5 g CS_2 (0.396 mL at 20 °C) to 10 mL with benzene.
4. Oxygen, purified.
5. Nitrogen, purified.
6. Hydrogen, prepurified.
7. Air, filtered compressed.

*See Special Precautions.

EQUIPMENT:

1. Sampler:
   a. Drying tubes: glass tube, 7 cm long, 6 mm OD, 4 mm ID; single, 270-mg section of granular anhydrous sodium sulfate between two silylated glass wool plugs. This removes moisture equivalent to 6 L of air at 100% RH and 22 °C.
   b. Sorbent tube: glass tube, 7 cm long, 6 mm OD, with flame-sealed ends containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Available commercially.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. PTFE tubing, 5-mm ID.
4. Gas chromatograph, flame photometric detector with sulfur filter, integrator and column (see page 1600-1).
   NOTE: A vent valve to vent the solvent peak after it elutes from the column is useful for manual injections.
5. Vials, glass, 25-mL, PTFE-lined crimp caps.
6. Volumetric flasks, 10-mL.
7. Syringe, 10-µL, readable to 0.1 µL.
8. Delivery pipet, 10-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C).

Benzene is a suspected human carcinogen. Work with these compounds only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing. Connect the drying tube to the front section of the charcoal tube with a 20-mm section of PTFE tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 3 to 25 L.
4. Keep the drying tube connected to the charcoal tube during shipping. Refrigerate (0 °C) to prevent CS_2 migration to the back section. Cap the open ends with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Detach and discard the drying tube. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 10 mL benzene to each vial. Attach crimp cap to each vial.
   NOTE 1: Smaller volumes of benzene, e.g., 1 mL, may also be used.
   NOTE 2: Toluene may be used in place of benzene with no decrease in desorption efficiency. However, the retention time for toluene is 30 min, which may be shortened by temperature programming.
7. Allow to stand 60 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.02 to 0.5 mg CS_2 per sample.
   a. Add known amounts of calibration stock solution to benzene in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph ([peak area]^2 vs. mg CS_2).
      NOTE: The FPD has a small linear range. Additional working standards may be required.
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg CS_2 recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1600-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE 1: Open the vent valve 2 to 3 min after injection to prevent exposure of the detector to benzene. Close the vent valve after benzene has eluted.
    NOTE 2: If peak area is above the linear range of the working standards, dilute with benzene, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of CS_2 found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of CS_2 in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:
Method S248 [4] was issued on January 30, 1976, and validated over the range 15 to 59 mg/m^3 using a 6-L sample with spiked samplers and atmospheres generated by syringe pump/triple air dilution and verified by total hydrocarbon analyzer [2]. Overall precision, s_r, was 0.059 with "found" concentrations 0.8% lower than "true" concentrations for 18 samples tested, representing a non-significant bias. Breakthrough (with drying tube preceding charcoal tube) occurred at 162 min (100% RH, 40 ppm, 0.2 L/min) = 32.4 L; DE (0.28 to 1.12 mg/sample) = 0.86; storage stability (0.56 mg/sample) = 85% after one week at 25 °C. At a 1 L/min sampling rate, breakthrough occurred at 19 L at 100 mg/m^3 [5]. A user check of this method gave recoveries an estimated LOD of 0.02 mg CS_2 per sample [6].

REFERENCES:
[1] Criteria for a Recommended Standard...Occupational Exposure to Carbon Disulfide, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-156 (1977).
[2] Documentation of the NIOSH Validation Tests, S248, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 1, P&CAM 179, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[4] Ibid, V. 3, S248, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[5] McCammon, C. S., P. M. Quinn and R. Kupel. A Charcoal Sampling Method and a Gas Chromatographic Analytical Procedure for Carbon Disulfide, Am. Ind. Hyg. Assoc. J., 36, 618-624 (1975).
[6] User check, UBTL, NIOSH Sequence #3990-L (unpublished, November 9, 1983).

METHOD REVISED BY: Mary Lynn Woebkenberg, NIOSH/DPSE; S248 originally validated under NIOSH Contract CDC-99-74-45.

CHLORINATED TERPHENYL (60% CHLORINE)

FORMULA: $C_{18}H_{4.65}Cl_{9.35}$ (average)
or
$C_6H_{(5-x)}Cl_xC_6H_{(4-y)}Cl_yC_6H_{(5-z)}Cl_z$
(x + y + z = 7 to 12)

METHOD: 5014
ISSUED: 2/15/84

M.W.: 552 (average) [2]

OSHA: no standard
NIOSH: no standard
ACGIH: no standard
(1 ppm ~23 mg/m³ @ NTP)

PROPERTIES: solid, d 1.67 g/mL @ 25 °C;
[2] BP 280 to 335 °C @ 5 mm Hg (0.67 kPa);
softening point 98 to 105.5 °C

SYNONYMS: chlorinated triphenyl, polychloroterphenyl, PCT, Aroclor 5460, CAS #11126-42-4.

SAMPLING

SAMPLER: FILTER
(glass fiber)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 100 L
-MAX: 1500 L

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.01 to 1.0 mg/m³ [1]
(100-L sample)

BIAS: none identified

OVERALL PRECISION (s_r): not evaluated

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ^{63}Ni ECD

ANALYTE: chlorinated terphenyl

DESORPTION: 4 mL isooctane, 30 min ultrasonic agitation

INJECTION VOLUME: 2 µL

TEMPERATURE-INJECTION: 240 °C
-DETECTOR: 300 °C
-COLUMN: 240 °C

GASES-CARRIER: nitrogen, 40 mL/min
-PURGE: nitrogen

COLUMN: 2.0 m x 2 mm ID glass; 3% QF-1 on 80/100 mesh Gas Chrom Q or equivalent

CALIBRATION: chlorinated terphenyl in isooctane

RANGE: 1 to 100 µg per sample [1]

ESTIMATED LOD: not determined

PRECISION (s_r): 0.081 [1]

APPLICABILITY: The working range is 0.001 to 0.1 mg/m³ for a 1000-L air sample.

INTERFERENCES: Presence of other chlorinated terphenyls, e.g., Aroclor 5442 (42% chlorine), or other substances with similar retention and detection characteristics may interfere with the analysis.

OTHER METHODS: None evaluated by NIOSH.

REAGENTS:

1. Isooctane (2,2,4-trimethylpentane), distilled in glass.*
2. Hexane, distilled in glass.*
3. Chlorinated terphenyl (60% chlorine).*
4. Calibration stock solution, 1 mg/mL. Dilute an accurately weighed 100 mg chlorinated terphenyl to 100 mL with hexane.
5. Nitrogen, 99.999%.

*See Special Precautions.

EQUIPMENT:

1. Sampler: 37-mm glass fiber filter (Gelman #64877 or equivalent) supported by a backup pad in a closed-face polystyrene cassette (Gelman #4338 or equivalent).
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Gas chromatograph, ^{63}Ni ECD, integrator and column (page 5014-1).
4. Tweezers, stainless steel.
5. Vials, glass, 5-mL, crimp seals or caps, silicone rubber septa lined with polyperfluoroethylene.
6. Pipets, 1-, 2- and 4-mL, with pipet bulb.
7. Ultrasonic bath.
8. Balance, readable to 0.1 mg.
9. Volumetric flasks, 5-, 10-, 25- and 100-mL.
10. Syringe, 10-µL.

SPECIAL PRECAUTIONS: Hexane (flash point = -22 °C) and isooctane (flash point = 4 °C) are highly flammable. Prepare samples and standards in well-ventilated hood.

Chlorinated terphenyls may be similar to chlorinated biphenyls in toxicity. Use protective clothing to avoid skin contact.

SAMPLING:

1. Calibrate the personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 100 to 1500 L.

SAMPLE PREPARATION:

3. Transfer filter to 5-mL vial using tweezers. Discard backup pad.
4. Pipet 4.0 mL of isooctane into vial and seal immediately.
5. Agitate vial in ultrasonic bath for 30 min to complete extraction.

CALIBRATION AND QUALITY CONTROL:

6. Calibrate daily with at least five working standards over the range 1 to 100 µg chlorinated terphenyl per sample.
   a. Add known amounts of calibration stock solution to hexane in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 9 and 10).
   c. Prepare calibration graph (detector response vs. chlorinated terphenyl).
7. Prepare two control samples at each of two levels for checking analysis of field samples.
   a. For each control sample, inject calibration stock solution directly onto filter. Mount filter in cassette and draw ca. 30 L of analyte-free air through (to evaporate hexane). Seal cassette and store overnight.
   b. Desorb filters as in steps 3 through 5, and analyze as in steps 9 and 10.
8. Check for possible contamination during shipment of field samples by comparing results from field blanks and media blanks.

MEASUREMENT:

9. Set gas chromatograph to conditions given on page 5014-1 and optimize detector performance per manufacturer's instructions. Using these conditions, retention time of largest and most distinct peak in cluster was about 6.1 min.
10. Inject sample aliquot and measure detector response, e.g., height from base of cluster to top of most prominent peak.

CALCULATIONS:

11. Read the mass, µg, of chlorinated terphenyl found in each sample (W) and average media blank (B) from calibration graph.
12. Calculate concentration, C (mg/m^3), of chlorinated terphenyl in the air volume sampled, V (L):

$$C = \frac{(W - B)}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Measurement precision was determined by analyzing spiked sampling media [1]. The average recovery was 1.006. There appeared to be no effect on recovery when up to 2700 L of charcoal-filtered air (40 °C and 40% relative humidity) was passed through filters spiked at the 1-µg level. Recoveries from 100-L samples collected from generated aerosol were 1.05 (s_r = 0.162) after seven days storage, and 0.875 (s_r = 0.206) after 14 days storage, relative to the amount found after one day. Generated concentrations were not reproducible, and independent methods for determining the true concentration appeared to provide lower and more imprecise results than this method. Because of the difficulty in determining the true concentration, overall precision and bias were not determined. Reference [1] provides additional information.

REFERENCES:

[1] Graham, M. M., and H. K. Dillon. Analytical Methods Evaluation and Validation for 1,2,4-Trichlorobenzene, 1,2,4,5-Tetrachlorobenzene, Pentachlorobenzene, and Polychlorinated Terphenyls: Research Report for Polychlorinated Terphenyls, NIOSH Contract No. 210-79-0102, Southern Research Institute, Birmingham, AL, available from NTIS (1982).

[2] Kimbrough, R. D., ed. "Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products," Topics in Environmental Health, V. 4, Elsevier/North-Holland Biomedical Press, Amsterdam, 20-21 (1980).

METHOD REVISED BY: R. Alan Lunsford, Ph.D., NIOSH/DPSE; data obtained under NIOSH Contract 210-79-0102.

FORMULA: $CH_2=CClCH=CH_2$; C_4H_5Cl

M.W.: 88.54

CHLOROPRENE

METHOD: 1002
ISSUED: 2/15/84

OSHA: 25 ppm (skin)
NIOSH: 1 ppm/15 min [1]
ACGIH: 10 ppm (skin)
(1 ppm = 3.62 mg/m³ @ NTP)

PROPERTIES: liquid; d = 0.958 g/mL @ 20 °C;
BP 58.9 °C; MP -130 °C;
VP 25 kPa (188 mm Hg; 25% v/v) @ 20 °C;
explosive range 4 to 20% v/v in air

SYNONYMS: beta-chloroprene; 2-chloro-1,3-butadiene; CAS# 126-99-8.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 1.5 L @ 25 ppm
-MAX: 8 L

SHIPMENT: no special precautions

SAMPLE STABILITY: at least 8 days @ 25 °C [1,2]

BLANKS: 2 to 10 field blanks per set

CAUTION: suspected carcinogen

ACCURACY

RANGE STUDIED: 44 to 174 mg/m³ [2]
(3-L samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.071 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: chloroprene

DESORPTION: 1 mL CS_2; let stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURES-INJECTION: 200 °C
-COLUMN: 125 °C
-DETECTOR: 250 °C

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: stainless steel, 6 m x 3 mm ID, 5% SP-1000 on 40/60 Chromosorb T or equivalent

CALIBRATION: solutions of distilled chloroprene in CS_2; hexane reference standard

RANGE: 0.1 to 0.6 mg per sample [1]

ESTIMATED LOD: 0.03 mg per sample

PRECISION (s_r): 0.021 [1,2]

APPLICABILITY: The working range is 10 to 60 ppm (40 to 200 mg/m³) for a 3-L air sample. The method is sensitive enough to determine concentrations as low as 12 ppm in 15-min samples taken at 0.2 L/min. NIOSH has sampled for chloroprene at two polychloroprene processing plants.

INTERFERENCES: None known.

OTHER METHODS: This is Method S112 with improved GC column, in a new format [3]. A similar method appears in the chloroprene criteria document [1].

Preceding page blank

REAGENTS:

1. Carbon disulfide, chromatographic quality.*
2. Chloroprene*, freshly distilled from xylene solution at reduced pressure; BP ≈ 31 °C at 354 mm Hg (47 kPa).
3. n-Pentane, reagent grade.
4. n-Hexane, reagent grade.
5. Calibration stock solution, 47.9 mg/mL. Deliver 0.500 mL (0.479 g at 20 °C) freshly distilled chloroprene from a delivery pipet under the surface of pentane in a partially-filled 10-mL volumetric flask. Dilute to the mark with pentane. Stable one day at -15 °C.
6. Nitrogen, purified.
7. Hydrogen, prepurified.
8. Air, filtered.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1002-1).
4. Micro-distillation apparatus for vacuum distillation of chloroprene.
5. Vials, 2-mL, glass with PTFE-lined septa and crimp seals.
6. Syringe, 10-µL, readable to 0.1 µL.
7. Volumetric flasks, 10-mL.
8. Pipets, 1-mL, graduated in 0.1 mL, with pipet bulb.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and flammable; work with it only in a hood.

Chloroprene incompatibilities by contact with oxidizers (e.g., peroxides) may cause polymerization with evolution of heat and rupture of containers. Chloroprene attacks some plastics, rubber and coatings. It will autoxidize very rapidly, even at 0 °C, producing an unstable peroxide (mixed 1,2- and 1,4-addition copolymer with oxygen) which catalyzes exothermic polymerization. Therefore, immediately after distilling store at -15 °C.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.05 L/min for a total sample size of 1.5 to 8 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL CS_2 to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.03 to 0.5 mg chloroprene per sample.
   a. Add known amounts of calibration stock solution below the surface of CS_2 in 10-mL volumetric flasks and dilute to the mark.

b. Analyze together with samples and blanks (steps 11 and 12).
c. Prepare calibration graph (peak area vs. mg chloroprene).

9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg chloroprene recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1002-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with CS_2, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of chloroprene found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of chloroprene in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S112 was issued on October 29, 1976, and validated over the range 44 to 175 mg/m^3 with eighteen 3-L samples from dynamically-generated test atmospheres, as well as a set of six samples at one times the OSHA standard level stored at room temperature for eight days to establish stability [2,4]. Eighteen more samples were spiked (six each at one-half, one and two times the the OSHA standard, 0.14 to 0.54 mg) directly. The pooled precision (s_r) for these three sets of analytical samples was 0.021. The average recovery for all three levels was 98.8%, representing a non-significant bias. The value for the taken concentration was obtained by monitoring during generation with a gas chromatograph with a 2-mL sampling loop. Bag standards were used to calibrate the gas chromatograph. The stored samples results were within 1% of samples analyzed after one day, indicating adequate storage stability for eight days. Six parallel breakthrough tubes were run at a time. The generated atmosphere was pulled through the charcoal tubes (critical orifices to control flow). Several breakthrough studies were done. With 94% relative humidity, breakthrough occurred at 30 min when sampling 0.194 L/min of 195 mg/m^3 (5.8 L). With 91% relative humidity, no breakthrough occurred after 240 min when sampling 0.045 L/min of 197 mg/m^3 (10.8 L).

REFERENCES:
[1] Criteria for a Recommended Standard-Occupational Exposure to Chloroprene, Appendices I and III, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-210 (1977).
[2] NIOSH Backup Data Report, S112, prepared under NIOSH Contract 210-76-0123, available as "Ten NIOSH Analytical Methods, Set 1," Order No. PB 271-712 from NTIS, Springfield, VA 22161.
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 2, S112, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[4] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY: Y. T. Gagnon, NIOSH/DPSE; S112 originally validated in NIOSH Contract 210-76-0123.

FORMULA: Cr

CHROMIUM and compounds, as Cr

METHOD: 7024
ISSUED: 2/15/84

M.W.: 52.00 (Cr); 152.02 (Cr_2O_3)

OSHA: 1.0 mg/m³ (metal; insoluble salts)*
0.5 mg/m³ (soluble salts)*
NIOSH: no standard*
ACGIH: 0.5 mg/m³ (soluble and insoluble)*
*Cr°, Cr(II), and Cr(III) only;
see Method 7600 for Cr(VI).

PROPERTIES: metal; d 7.14 g/cm³;
MP 1890 °C; valences +1 to +6 in salts

SYNONYMS: vary depending on the compound; CAS #7440-47-3 (Cr metal); CAS #1308-38-9 (Cr_2O_3).

SAMPLING

SAMPLER: FILTER
(0.8-µm cellulose ester membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 10 L @ 0.5 mg/m³
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.4 to 1.8 mg/m³ (insoluble) [5]
0.3 to 1 mg/m³ (soluble) [5]
(90-L samples)

BIAS: not significant [5]

OVERALL PRECISION (s_r): 0.076 (insoluble) [5]
0.085 (soluble [5]

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, FLAME

ANALYTE: chromium

ASHING: conc. HCl, 9 mL; 140 °C
conc. HNO_3, 9 mL; 400 °C

FINAL SOLUTION: 5% HNO_3, 20 mL

FLAME: nitrous oxide-acetylene, reducing

WAVELENGTH: 357.9 nm

CALIBRATION: solutions of Cr in 5% HNO_3

RANGE: 5 to 250 µg per sample [3,4]

ESTIMATED LOD: 0.06 µg per sample [1]

PRECISION (s_r): 0.04 to 0.06 [5]

APPLICABILITY: The working range is 0.05 to 2.5 mg/m³ for a 100-L air sample. This is an elemental analysis for total Cr, not compound specific. Some compounds of Cr may not be dissolved by this method. Aliquots can be analyzed separately for approximately four additional metals.

INTERFERENCES: Interferences from iron and nickel are minimized by using a high temperature flame (reducing nitrous oxide-acetylene or oxidizing air-acetylene).

OTHER METHODS: This method combines and replaces P&CAM 173 [1], P&CAM 152 [2], S323 [3], and S352 [4]. Method 7300 (ICP-AES) is an alternate analytical method. Hexavalent chromium, sampled on PVC filters, may be determined colorimetrically by Method 7600. Method 7200 gives an XRF determination of chromium in welding and brazing fumes.

REAGENTS:

1. Nitric acid, conc.
2. Hydrochloric acid, conc.
3. Nitric acid, 5%. Add 50 mL conc. HNO_3 to water; dilute to 1 L.
4. Calibration stock solution, 1000 µg Cr/mL. Dissolve 3.735 g K_2CrO_4 or 2.829 g $K_2Cr_2O_7$ in distilled or deionized water to make 1 L solution.
5. Distilled or deionized water.
6. Nitrous oxide.
7. Acetylene.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-µm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with a nitrous oxide-acetylene burner head and chromium hollow cathode lamp.
4. Regulators, two-stage, for nitrous oxide and acetylene.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.*
6. Volumetric flasks, 100-mL.*
7. Graduated centrifuge tubes, 15-mL.*
8. Assorted volumetric pipets, as needed.*
9. Hotplate, surface temperature to 400 °C.

*Clean all glassware with nitric acid and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Perform all acid digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a sample size of 10 to 1000 L. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

NOTE: The following sample preparation gave quantitative recovery (see EVALUATION OF METHOD) [3,4]. Steps 4 through 9 of Method 7300 or other quantitative ashing techniques may be substituted, especially if several metals are to be determined on a single filter.

3. Open the cassettes and filter holders and transfer the samples and blanks to clean beakers.
4. Add 3 mL conc. HCl, cover with a watchglass, heat on hotplate (140 °C) until the volume is reduced to ca. 0.5 mL. Repeat two more times using 3 mL conc. HCl.
   NOTE: Start reagent blanks at this step.
5. Add 3 mL conc. HNO_3, cover with a watchglass, heat on hotplate (140 °C) until the volume is reduced to ca. 0.5 mL. Repeat two more times using 3 mL conc. HNO_3.
6. Heat on hotplate (400 °C) until a white ash appears.
7. Cool solution and dissolve the residues in 1 mL conc. HNO_3.
8. Transfer the solution quantitatively to a 15-mL graduated centrifuge tube.
9. Dilute to volume with distilled water.

CALIBRATION AND QUALITY CONTROL:

10. Add known amounts of calibration stock solution, covering the range 0 to 1000 µg Cr (0 to 200 µg Cr per sample) to 100-mL volumetric flasks and dilute to volume with 5% HNO_3.
11. Analyze the working standards together with the blanks and samples (steps 16 and 17).

12. Prepare a calibration graph of absorbance vs. solution concentration (µg/mL).
13. Aspirate a standard for every 10 samples to check instrument drift.
14. Check analytical recoveries with at least one spiked media blank per 10 samples.
15. Use method of additions occasionally to check for interferences.

MEASUREMENT:

16. Set spectrophotometer as recommended by the manufacturer and to conditions on page 7024-1.
    NOTE: Air-acetylene flame may also be used. In a fuel-lean air-C_2H_2 or reducing (fuel-rich) N_2O-C_2H_2 flame, interference by Fe or Ni is minimized or eliminated, but sensitivity for Cr is reduced. A reducing air-C_2H_2 flame provides the best sensitivity, but the greatest susceptibility to interference [6].
17. Aspirate standards and samples. Record absorbance readings
    NOTE: If the absorbance values for the samples are above the linear range of the standards, dilute the solutions with 5% HNO_3, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

18. Using the measured absorbances, calculate the corresponding solution concentrations (µg/mL) of chromium in the sample, C_s, and average media blank, C_b, from the calibration graph.
19. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration of chromium, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Lab testing with spiked filters and generated atmospheres of soluble chromium (potassium dichromate) was done at one-half, one and two times the OSHA standard of 0.5 mg/m^3. The range studied was 0.28 to 0.95 mg/m^3. The precision was 0.082 and a bias was not observed [3,5].

Lab testing with spiked filters and generated atmospheres of insoluble chromium, (produced from thermal decomposition of chromium hexacarbonyl) was done at one-half, one and two times the OSHA standard of 1.0 mg/m^3 [4,5]. Collection efficiency was 1.00 and analytical recoveries averaged 98% in the range 45 to 190 µg Cr per sample.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd ed., V. 5, P&CAM 173, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[2] Ibid, V. 1., P&CAM 152, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[3] Ibid, V. 3, S323, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[4] Ibid, S352.
[5] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[6] Analytical Methods for Atomic Aborption Spectrophotometry, Perkin-Elmer (1976).

METHOD REVISED BY: Mark Millson and R. Delon Hull, NIOSH/DPSE; Methods S323 and S352 developed under NIOSH Contract CDC-99-74-45.

FORMULA: CrO_3; CrO_4^{-2}; $Cr_2O_7^{-2}$

CHROMIUM, HEXAVALENT

METHOD: 7600

M.W.: 52.00 (Cr); 115.99 (CrO_4^{-2}); 215.99 ($Cr_2O_7^{-2}$)

ISSUED: 2/15/84

OSHA: 0.1 mg/m³

NIOSH: 0.025 mg/m³ (soluble chromates);
0.001 mg/m³ (carcinogenic chromates) [1]

ACGIH: 0.050 mg/m³; some insoluble chromates are carcinogens

PROPERTIES: oxidizing agent

SYNONYMS: vary depending upon the compound; CAS #1333-82-0 (chromic acid; chromium trioxide).

SAMPLING

SAMPLER: FILTER
(5.0-µm PVC membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 8 L @ 0.025 mg/m³
-MAX: 400 L

SHIPMENT: routine

SAMPLE STABILITY: analyze within 2 weeks

BLANKS: 2 to 10 field blank per set

ACCURACY

RANGE STUDIED: 0.5 to 10 µg/m³

BIAS: not significant

OVERALL PRECISION (s_r): 0.084 [3]

MEASUREMENT

TECHNIQUE: VISIBLE ABSORPTION SPECTROPHOTOMETRY

ANALYTE: CrO_4^{-2}-diphenylcarbazide complex

WAVELENGTH: 540 nm

EXTRACTION SOLUTION: 0.5 N H_2SO_4 or 2% NaOH-3% Na_2CO_3 (see APPLICABILITY and steps 4 and 5)

CALIBRATION: solutions of Cr(VI) in 0.5 N H_2SO_4

RANGE: 0.2 to 10 µg per sample

ESTIMATED LOD: 0.05 µg per sample

PRECISION (s_r): 0.029 [4]

APPLICABILITY: The working range is 0.001 to 0.05 mg/m³ for a 200-L air sample. This method may be used for the analysis of insoluble or soluble Cr(VI). Depending on the solubility of the Cr(VI) compound, either NaOH-Na_2CO_3 or 0.5 N H_2SO_4 will be used as extraction solution. The NaOH-Na_2CO_3 solution performs a more complete extraction [4].

INTERFERENCES: Possible interferences are iron, copper, nickel, and vanadium; 10 µg of any of these causes an absorbance equivalent to about 0.02 µg Cr(VI) due to formation of colored complexes. Interference due to reducing agents (e.g., Fe, Fe^{++}) is minimized by alkaline extraction (step 5).

OTHER METHODS: This method combines and replaces P&CAM 169 [2], S317 [3] and P&CAM 319 [4]; the Cr(VI) criteria document [1] contains a method similar to P&CAM 169.

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REAGENTS:

1. Sulfuric acid, conc. (98% w/w).
2. Sulfuric acid, 6 N. Add 167 mL conc. H_2SO_4 to water in a 1-L flask; dilute to the mark.
3. Sulfuric acid, 0.5 N. Add 14.0 mL conc. H_2SO_4 to water in a 1-L flask; dilute to the mark.
4. Sodium carbonate anhydrous.
5. Sodium hydroxide.
6. Potassium chromate.
7. Diphenylcarbazide solution. Dissolve 500 mg sym-diphenylcarbazide in 100 mL acetone and 100 mL water.
8. Cr(VI) standard, 1000 µg/mL.*
9. Calibration stock solution, 10 µg/mL. Dilute 1000 µg/mL Cr(VI) standard 1:100 with deionized water.
10. Filter extraction solution, 2% NaOH-3% Na_2CO_3. Dissolve 20 g NaOH and 30 g Na_2CO_3 in deionized water to make 1 L of solution.
11. Nitrogen, compressed.

*See Special Precautions.

EQUIPMENT:

1. Sampler: polyvinyl chloride filter, 5.0-µm pore size, 37-mm diameter in polystyrene cassette filter holder (FWSB [MSA] or VM-1 [Gelman] or equivalent).
   NOTE: BSWP PVC filters (Millipore) are not acceptable for sampling Cr(VI). This filter has been found to reduce a significant amount of an aqueous 5 µg Na_2CrO_4 spike within 24 hrs.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Bottles, 20-mL glass, PTFE-lined, screw cap.*
4. Forceps, plastic.
5. Spectrophotometer, UV-visible, with cuvettes, 5-cm path length.
6. Filtration apparatus, vacuum.*
7. Beakers, borosilicate, 50-mL.*
8. Watchglass.*
9. Volumetric flasks, 25-, 100- and 1000-mL.*
10. Hotplate, 120 to 400 °C.
11. Micropipette, 20-µL and other sizes.
12. Centrifuge tubes, 40-mL, graduated, with plastic stoppers.*
13. Buchner funnel.*

*Clean all glassware with 1:1 HNO_3 and rinse thoroughly before use.

SPECIAL PRECAUTIONS: Insoluble chromates are suspected human carcinogens [1]. All work should be performed in a hood.

SAMPLING:

1. Calibrate the sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate in the range 1 to 4 L/min for a sample size of 2 to 400 L. Do not exceed 1 mg total dust loading on the filter.
3. Remove the PVC filter from the cassette within 1 hr of completion of sampling and place it in a 20-mL bottle. Handle the filter only with forceps. Discard the backup pad.

SAMPLE PREPARATION:

NOTE: There are two sample preparation techniques outlined below. For soluble chromates or chromic acid, follow step 4; for insoluble chromate or Cr(VI) in the presence of Fe, Fe^{++} or other reducing agents, follow step 5.

4. Sample preparation for soluble chromates and chromic acid.
   a. Remove the blank and sample filters from the bottle, then fold and place them into a 40-mL graduated centrifuge tube.

b. Add 6 or 7 mL 0.5 N H_2SO_4 to each tube and shake it to wash all surfaces of the filter. Remove the filter from the tube with plastic forceps, carefully washing all surfaces with an additional 1 to 2 mL 0.5 N H_2SO_4. Discard the filters. Start reagent blanks at this point.

c. Filter the solution to remove interferences from suspended dust through a moistened PVC filter in a Buchner funnel. Rinse the bottle, which contained the filter, with 2 to 3 mL of the acid and pour into the funnel. Filter the sample solution and rinse the funnel and filter with 5 to 8 mL 0.5 N H_2SO_4. Add 0.5 mL diphenylcarbazide solution to each centrifuge tube. Bring the total volume in each centrifuge tube to 25 mL with 0.5 N H_2SO_4. Shake to mix and allow a few minutes for the color to develop. Transfer the solution to a clean 5-cm cuvette and analyze (steps 9 through 11).

5. Sample preparation for insoluble chromates and for Cr(VI) in the presence of iron or other reducing agents:

NOTE: If significant amounts of Cr(III) are expected to be present, degas the sample solution before proceeding and purge the headspace above the solution during step 5.a.

a. Remove the PVC filter from the bottle, place it in a 50-mL beaker, and add 5.0 mL filter extraction solution, 2% NaOH - 3% Na_2CO_3. Start reagent blanks at this point. Purge the headspace above the solution with nitrogen throughout the extraction process to avoid oxidation of any Cr(III). Cover the beaker with a watchglass and heat it to near the boiling point on a hotplate with occasional swirling for 30 to 45 min. Do not boil the solution or heat longer than 45 min. Do not allow the solution to evaporate to dryness because hexavalent chromium may be lost due to reaction with the PVC filter. An indication that hexavalent chromium has been lost in this manner is a brown-colored PVC filter.

b. Cool the solution and transfer it quantitatively with distilled water rinses to a 25-mL volumetric flask, keeping the total volume about 20 mL.

NOTE: If the solution is cloudy, filter it through a PVC filter in a vacuum filtration apparatus using distilled water rinses.

c. Add 1.90 mL 6 N sulfuric acid to the volumetric flask and swirl to mix.

CAUTION: CARBON DIOXIDE WILL BE EVOLVED CAUSING INCREASED PRESSURE IN THE FLASK. LET THE SOLUTION SIT FOR SEVERAL MINUTES UNTIL VIGOROUS GAS EVOLUTION CEASES.

d. Add 0.5 mL diphenylcarbazide solution, dilute to the mark with distilled water and invert several times to mix thoroughly. Pour out about one-half of the contents of the flask, stopper the flask and shake it vigorously several times, removing the stopper each time to relieve pressure.

NOTE: This step releases bubbles of carbon dioxide which would otherwise cause high and erratic readings.

CALIBRATION AND QUALITY CONTROL:

6. Transfer 6 or 7 mL 0.5 N H_2SO_4 to each of a series of 25-mL volumetric flasks. Pipet 0 to 100 µL of 10 µg/mL calibration stock solution into the volumetric flasks. Add 0.5 mL diphenylcarbazide solution to each and sufficient 0.5 N H_2SO_4 to bring the volume to 25 mL. These working standards contain 0 to 1.0 µg Cr(VI).
7. Analyze the working standards (steps 9 through 11).
8. Prepare a calibration graph [absorbance vs. µg Cr(VI)].

MEASUREMENT:

9. Set wavelength on the spectrophotometer to 540 nm.
10. Set to zero using a 0.5 N H_2SO_4 reagent blank.

11. Transfer sample solution to a 5-cm cuvette and record the absorbance.
    NOTE: If the absorbance values for the samples are higher than the standards, dilute using 0.5 N H_2SO_4 and multiply the resulting absorbance by the appropriate dilution factor.

CALCULATIONS:

12. From the calibration graph, determine the mass of Cr(VI) in each sample, W (µg), and in the average blank, B (µg).
13. Calculate the concentration, C (mg/m^3), of Cr(VI) in the air volume sampled, V (L):

$$C = \frac{W - B}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

P&CAM 169 and S317 are essentially the same method and are suitable for soluble chromate and chromic acid. Method S317 was validated with generated samples of chromic acid mist [3,5], and P&CAM 169 was tested with field samples [2,6]. P&CAM 319 was developed because a method was needed to analyze for insoluble chromates [4]. This method was tested with insoluble chromates in matrices such as paints, primer and ceramic powders [4].

Precision, analytical range, recovery data, etc., for the three methods pooled are as follows:

Total s_r:	0.084
Measurement s_r [2,3,4]:	0.02 to 0.04
Range [4]:	0.5 to 10 µg/m^3
Collection Efficiency [5]:	94.5%
Sampling Rate [2,3,4]:	1.5 to 2.5 L/min
Stability (two weeks) [2]:	96% recovery
Acceptable Filters [4]:	FWSB (MSA); VM-1 (Gelman).

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Cr(VI), 171-176, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-129 (1976).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 169, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[3] Ibid, V. 3, S317, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[4] Ibid, V. 6, P&CAM 319, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).
[5] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[6] Abell, M. T. and J. R. Carlberg. A Simple Reliable Method for the Determination of Airborne Hexavalent Chromium, Am. Ind. Hyg. Assoc. J., 35, 229 (1974).

METHOD REVISED BY: Daniel Molina and Martin T. Abell, NIOSH/DPSE; Method S317 validated under NIOSH Contract CDC-99-74-45.

FORMULA: Co

M.W.: 58.93 (Co); 74.93 (CoO)

COBALT and compounds, as Co

METHOD: 7027
ISSUED: 2/15/84

OSHA: 0.1 mg/m³
NIOSH: not established
ACGIH: 0.1 mg/m³ (fume, dust)

PROPERTIES: magnetic, hard metal; valence 2, 3; MP 1495 °C; VP not significant

SYNONYMS: vary depending upon the compound; CAS #7440-48-4 (Co); CAS #1307-96-6 (CoO).

SAMPLING

SAMPLER: FILTER
(0.8-µm cellulose ester membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 30 L @ 0.1 mg/m³
-MAX: 1500 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.03 to 0.26 mg/m³ [4]
(270-L samples)

BIAS: not significant [4]

OVERALL PRECISION (s_r): 0.071 (dust) [4];
0.069 (fume) [4]

MEASUREMENT

!
!TECHNIQUE: ATOMIC ABSORPTION, FLAME
!
!ANALYTE: cobalt
!
!ASHING: aqua regia, 3 mL, 140 °C;
! conc. HNO_3, 6 mL, 140 °C;
! room temperature, 30 min;
! 140 °C to near dryness
!
!FINAL SOLUTION: 5% HNO_3, 10 mL
!
!FLAME: air-acetylene, oxidizing
!
!WAVELENGTH: 240.7 nm
!
!BACKGROUND CORRECTION: D_2 or H_2 lamp
!
!CALIBRATION: Co^{++} in 5% HNO_3
!
!RANGE: 3 to 90 µg per sample [2]
!
!ESTIMATED LOD: 0.6 µg per sample [5]
!
!PRECISION (s_r): 0.03 [4]; 0.02 [5]
!

APPLICABILITY: The working range is 0.01 to 0.3 mg/m³ for a 300-L sample. This is an elemental analysis, not compound specific. Verify that the types of compounds in the samples are soluble with this ashing procedure. Aliquots of the samples can be analyzed separately for approximately four additional metals.

INTERFERENCES: The use of D_2 or H_2 continuum background correction is required to control molecular or flame absorption. There are no known spectral line interferences.

OTHER METHODS: This method combines and replaces P&CAM 173 [1] and S203 [2] for cobalt. Method 7300 (ICP-AES) is an alternate analytical technique.

REAGENTS:

1. Nitric acid, conc.
2. Hydrochloric acid, conc.
3. Aqua regia: mix 3 volumes conc. HCl with 1 volume conc. HNO_3.
4. Nitric acid, 5% (w/v). Add 50 mL conc. HNO_3 to water; dilute to 1 L.
5. Calibration stock solution, 1000 µg Co/mL. Commercially available or dissolve 1.000 g Co metal in minimum volume of aqua regia. Dilute to 1 L with 5% HNO_3.
6. Distilled or deionized water.
7. Air, filtered.
8. Acetylene.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-µm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with an air-acetylene burner head and cobalt hollow cathode lamp.
4. Regulators, two-stage, for air and acetylene.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.*
6. Volumetric flasks, 10- and 100-mL.*
7. Micropipets, 5 to 60 µL.*
8. Hotplate, surface temperature 140 °C.

*Clean with conc. HNO_3 and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Perform all acid digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative filter in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a sample size of 30 to 1500 L. Do not exceed a filter loading of approximately 2 mg total dust.

SAMPLE PREPARATION:

NOTE: The following sample preparation gave quantitative recovery (see EVALUATION OF METHOD). Steps 4 through 9 of Method 7300 or other quantitative ashing techniques may be substituted, especially if several metals are to be determined on a single filter.

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
4. Add 3 mL aqua regia, cover with a watchglass, let stand at room temperature 30 min. Start reagent blanks at this point.
5. Heat on hotplate (140 °C) until most of the acid has evaporated (ca. 0.5 mL remains).
6. Repeat 2 more times using 3 mL conc. HNO_3 each time. Leave about 1 mL solution after the last digestion.
7. Cool each beaker, remove watchglass, and rinse into the beaker with 5% HNO_3.
8. Dissolve the residues in 2 to 3 mL 5% HNO_3.
9. Transfer the solution quantitatively to a 10-mL volumetric flask.
10. Dilute to volume with 5% HNO_3.

CALIBRATION AND QUALITY CONTROL:

11. Add known amounts, covering the expected range of samples (0 to 60 µg Co per sample), of calibration stock solution to 10-mL volumetric flasks and dilute to volume with 5% HNO_3.
12. Analyze the working standards together with the blanks and samples (steps 17 and 18).
13. Prepare a calibration graph of absorbance vs. solution concentration (µg/mL).
14. Aspirate a standard for every 10 samples to check instrument drift.

15. Check recoveries with at least one spiked media blank per 10 samples.
16. Use method of additions occasionally to check for interferences.

MEASUREMENT:

17. Set spectrophotometer according to the manufacturer's recommendations and to the conditions on page 7027-1.
18. Aspirate standards and samples. Record absorbance readings.
    NOTE: If the absorbance values for the samples are above the linear range of the standards, dilute the solutions with 5% HNO_3, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

19. Using the measured absorbances, calculate the corresponding concentrations (µg/mL) of cobalt in the sample, C_s, and average media blank, C_b, from the calibration graph.
20. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration, C (mg/m^3), of cobalt in the volume of air sampled, V (L):

$$C = \frac{(C_s V_s - C_b V_b)}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method S203 [2] was issued on February 18, 1977, and validated over the range 0.03 to 0.22 mg/m^3 Co fume and 0.04 to 0.26 mg/m^3 Co dust using spiked filters and generated atmospheres of cobalt dust and fume (Co_2O_3) [4]. Precision and accuracy data are given on page 7027-1.

A separate check on this method showed 98% recovery from filters spiked with 12 or 96 µg Co [5].

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd ed., V. 5, P&CAM 173, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[2] Ibid, V. 4, Method S203, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[3] Analytical Methods for Atomic Absorption Spectrophotometry, Perkin-Elmer (1976).
[4] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[5] User check, UBTL, NIOSH Seq. #3990-N (unpublished, November 29, 1983).

METHOD REVISED BY: Mark Millson and R. DeLon Hull, NIOSH/DPSE; S203 originally validated under NIOSH Contract CDC-99-74-45.

FORMULA: Cu

M.W.: 63.54

COPPER (dust and fume)

Method: 7029
ISSUED: 2/15/84

OSHA: 0.1 mg/m³ (fume); 1 mg/m³ (dust)
NIOSH: no standard
ACGIH: 0.2 mg/m³ (fume);
1 mg/m³, STEL 2 mg/m³ (dust, mist)

PROPERTIES: soft metal; valence +1, +2 in salts
MP 1083 °C

SYNONYMS: vary depending upon the compound; CAS #7440-50-8 (Cu); CAS #1317-39-1 (Cu_2O), CAS #1317-38-0 (CuO).

SAMPLING

SAMPLER: FILTER
(0.8-µm cellulose ester membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 50 L @ 0.1 mg/m³
-MAX: 1500 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.05 to 0.59 mg/m³ (fume) [5,6]
0.47 to 1.8 mg/m³ (dust) [4]

BIAS: not significant [4,5,6]

OVERALL PRECISION (s_r): 0.044 (fume) [5,6];
0.051 (dust) [4]

MEASUREMENT

!TECHNIQUE: ATOMIC ABSORPTION, FLAME

!ANALYTE: copper

!ASHING: conc. HNO_3, 6 mL, 140 °C;
! conc. HCl, 6 mL, 400 °C

!FINAL SOLUTION: 0.5 N HCl; 25 mL

!FLAME: air-acetylene, oxidizing

!WAVELENGTH: 324.7 nm

!BACKGROUND CORRECTION: not required

!CALIBRATION: Cu^{++} in 0.5 N HCl

!RANGE: 5 to 125 µg per sample [2]

!ESTIMATED LOD: 0.05 µg per sample [1]

!PRECISION (s_r): 0.03 [1,4,5]

APPLICABILITY: The working range is 0.05 to 1.3 mg/m³ for a 100-L air sample. This is an elemental analysis, applicable to either dust or fume, with an additional separation step to quantitate soluble copper dust (e.g., $CuSO_4$) in the presence of copper fume. Aliquots of the samples can be analyzed separately for many additional metals.

INTERFERENCES: Background correction is not required. Interferences to the fume/soluble dust separation step include insoluble copper compounds and copper compounds such as copper acetate which form insoluble hydroxides when dissolved in water.

OTHER METHODS: This method combines and replaces P&CAM 173 [1], S354 [2], and S186 [3]. Method 7300, plasma emission (ICP-AES), is an alternate method.

Preceding page blank 167

REAGENTS:

1. Nitric acid, conc.
2. Hydrochloric acid, conc.
3. Hydrochloric acid, 0.5 N. Add 41.5 mL conc. HCl to water, dilute to 1 L.
4. Calibration stock solution, 1000 µg/mL. Commercially available, or dissolve 1.000 g Cu metal in minimum volume of (1+1) HNO_3. Dilute to 1 L with 0.5 N HCl.
5. Distilled-deionized water.
6. Air, filtered.
7. Acetylene.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-µm pore size, 37 mm-diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with an air-acetylene burner head and copper hollow cathode lamp and two-stage regulators for air and acetylene.
4. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.*
5. Volumetric flasks, 25-mL.*
6. Assorted volumetric pipets, as needed.*
7. Hotplate, surface temperature 140 °C and 400 °C.
8. Equipment for fume/dust separation step:
   a. cellulose ester membrane filters, 47-mm, 0.3-µm pore size (Millipore PHWP or equivalent);
   b. cellulose ester membrane filter, 47-mm, 5-µm pore size (Gelman GA-1 or equivalent);
   c. filtration apparatus (Gelman No. 1107 or equivalent).

*Clean all glassware with conc. nitric acid and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Perform all acid digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a sample size of 50 to 1500 L. Do not exceed a total filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

NOTE: The following sample preparation gave quantitataive recovery (see EVALUATION OF METHOD). Other quantitative ashing techniques (e.g., HNO_3-$HClO_4$ [Method 7300]) may be useful alternatives, especially if several metals are to be determined on a single filter.

3. Proceed to step 4 if fume/dust separation is not desired. For fume/dust separation:
   a. Using forceps, prewet a 47-mm, 0.3-µm pore size cellulose ester membrane filter by placing it on the surface of distilled water. Remove the filter, tap off excess water, and mount it on the filtration unit.
   b. Transfer the sample filter from the cassette filter holder to the filtration unit, placing it concentrically on top of the 47-mm filter with the fume deposit up.
   c. Apply and release the vacuum so that the 37-mm filter is gently wetted from the moisture retained on the 47-mm filter. This also insures the removal of any air bubbles between the filters.
   d. When the fume is visually clear of air bubbles and wet throughout, apply a vacuum of 10 to 15 PSIG (69 to 103 kPa). Release the vacuum.

e. Place a 47-mm, 5-μm cellulose ester membrane filter on the surface of water to wet it, remove excess water by blotting with tissue, and place it concentrically on top of the 37-mm filter. Press the surface of the top filter with a clean tissue to ensure that no air bubbles remain between any of the filters.

f. Mount the upper part of the filtration unit, add 5 mL of distilled water, and allow vacuum to draw water through the filters. Repeat with 5 mL more water. Combine the filtrates, which contain soluble copper compounds, in a clean beaker. Start reagent blanks at this point.

g. Transfer all filters to a clean beaker. Proceed to step 5.
NOTE: Each sample blank is a combination of three filters.

4. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
5. Add 6 mL conc. HNO_3. Cover with a watchglass and heat on hotplate (140 °C) until the volume is reduced to approximately 0.5 mL. Repeat two more times using 2 mL conc. HNO_3 each time.
NOTE: Start reagent blanks at this point if step 3 was omitted.
6. Add 2 mL conc. HCl, cover with a watchglass, heat on hotplate (400 °C) until the volume is reduced to approximately 0.5 mL. Repeat two more times using 2 mL conc. HCl. Do not allow the solution to go to dryness at any point.
7. Cool solution and add 10 mL distilled water.
8. Transfer the solution quantitatively to a 25-mL volumetric flask. Dilute to volume with distilled water.

CALIBRATION AND QUALITY CONTROL:

9. Add known amounts, covering the range 0 to 125 μg Cu per sample, of calibration stock solution to 25-mL volumetric flasks and dilute to volume with 0.5 N HCl.
10. Analyze the working standards together with the blanks and samples (steps 15 and 16).
11. Prepare a calibration graph by plotting absorbance versus solution concentration (μg/mL).
12. Aspirate a standard for every 10 samples to check instrument drift.
13. Check analytical recoveries with at least one spiked media blank per 10 samples.
14. Use method of additions occasionally to check for interferences.

MEASUREMENT:

15. Set spectrophotometer as specified by the manufacturer and to conditions on page 7029-1.
16. Aspirate standards, samples, and blanks. Record absorbance readings.
NOTE: If the absorbance values for the samples are above the linear range of the standards, dilute the sample solutions with 0.5 N HCl, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

17. Using the measured absorbances, calculate the corresponding concentrations (μg/mL) of copper in the sample, C_s, and average media blank, C_b, from the calibration graph.
18. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration of copper in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:
Method S186 was validated on August 29, 1975, with overall sampling and analytical precision, s_r = 0.051, over the range 0.47 to 1.8 mg/m³ for a 90-L sample of CuO dust [3,4] and Method S354 was validated on September 30, 1977, with overall sampling and analytical precision, s_r = 0.058, over the range 0.05 to 0.37 mg/m³ for a 480-L sample of Cu fume [2,5]. Copper fume atmospheres were generated by thermal decomposition and subsequent oxidation of cupric acetate aerosol. The size of the copper fume was 0.04 to 0.14 µm by electron microscopy and the collection efficiency of the sampler for this fume was 1.00 [2,5,9].

The dust-fume separation step was evaluated with samples laden with copper fume generated from copper welding; the samples were then placed into a dust generation system and overlaid with a known deposition of copper sulfate dust. With a dust loading of about 600 µg $CuSO_4$ and fume concentrations of 0.13 to 0.59 mg/m³, an average of 96.5% of the dust was removed. The analysis of the copper fume had a pooled s_r of 4.4% with an average bias of 5.3% [6].

Efficiencies of removal of Cu dust and fume were determined from samples containing only dust or only fume. Measured efficiencies were: (1) from filters containing 213 to 265 µg $CuSO_4$, an average of 97.8% was removed using 10 to 50 mL water; (2) filters laden with ca. 200 µg Cu/filter lost 11.5% Cu after washing with 10 mL H_2O. Because the non-equilibrium nature of the washing process does not lend itself to accurate prediction of the amount of copper fume removed by the wash water, no correction factor for the amount of fume removed was determined or employed. The elemental analysis used in the evaluation did not distinguish between copper from the fume and from the dust [6].

REFERENCES:
[1] NIOSH Manual of Analytical Methods, 2nd ed., V. 5, P&CAM 173, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[2] Ibid, V. 4, Method S354, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[3] Ibid, V. 3, Method S186, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[4] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[5] Backup Data Report for Copper Fume, S354, prepared under NIOSH Contract No. 210-76-0123, available as "Ten NIOSH Analytical Methods, Set 5," Order No. PB 287-499 from NTIS, Springfield, VA 22101.
[6] Carsey, T. Development of a Sampling and Analytical Method for Copper Fume, final report, NIOSH (DPSE) (unpublished, September, 1982).
[7] Winefordner, J. D., Ed. Spectrochemical Methods of Analysis, John Wiley & Sons (1971).
[8] Analytical Methods for Atomic Absorption Spectrophotometry, Perkin-Elmer (1976).
[9] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY: Mark Millson, R. DeLon Hull, and Thomas P. Carsey, Ph.D., NIOSH/DPSE; originally validated under NIOSH Contracts CDC-94-74-45 and 210-76-0123.

FORMULA: OH; C_7H_8O

CH_3

M.W.: 108.13

CRESOL, all isomers

METHOD: 2001
ISSUED: 2/15/84

OSHA: 5 ppm
NIOSH: 10 mg/m³ [1]
ACGIH: 5 ppm (skin)
(1 ppm = 4.42 mg/m³ @ NTP)

PROPERTIES: Table 1

SYNONYMS: o-cresol: 2-methylphenol; CAS #95-48-7.
m-cresol: 3-methylphenol; CAS #108-39-4.
p-cresol: 4-methylphenol; CAS #106-44-5.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(silica gel, 150 mg/75 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 5 L @ 5 ppm
-MAX: 20 L

SHIPMENT: routine

SAMPLE STABILITY: at least 1 week @ 25 °C [2]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 10 to 42 mg/m³ [2]
(20-L samples)

BIAS: not signficant [2]

OVERALL PRECISION (s_r): 0.068 [2]

MEASUREMENT

!
!TECHNIQUE: GAS CHROMATOGRAPHY, FID
!
!ANALYTE: cresol isomers
!
!DESORPTION: 1 mL acetone; stand 30 min
!
!INJECTION VOLUME: 5 µL
!
!TEMPERATURE-INJECTION: 230 °C
! -DETECTOR: 250 °C
! -COLUMN: 200 °C
!
!CARRIER GAS: N_2 or He, 50 mL/min
!
!COLUMN: stainless steel, 3 m x 3 mm, 10% FFAP on
! 80/100 mesh, acid-washed DMCS
! Chromosorb W or equivalent
!
!CALIBRATION: solutions of the cresol (all
! isomers) mixture in acetone
!
!RANGE: 0.1 to 1.2 mg per sample
!
!ESTIMATED LOD: not determined
!
!PRECISION (s_r): 0.028 [2]
!

APPLICABILITY: The working range is 5 to 60 mg/m³ for a 20-L air sample.

INTERFERENCES: Silica gel has a high affinity for water and will have greatly reduced capacity at high humidity.

OTHER METHODS: This method is a revision of S167 [3].

REAGENTS:

1. Acetone, chromatographic quality.
2. n-Hexane.
3. Cresol (all isomers).* Prepare standard mixture of 20 g ortho-, 40 g meta- and 30 g para- and mix.
4. Calibration stock solution, 104 mg/mL. Dilute 1040 mg cresol isomer mixture (1.0 mL at 20 °C) to 10 mL with n-hexane.
5. Hydrogen, prepurified.
6. Nitrogen, purified.
7. Air, filtered.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID; two sections of 20/40 mesh silica gel separated by a 2-mm portion of urethane foam (front = 150 mg, back = 75 mg).
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 2001-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Pipet, 1.0-mL, with pipet bulb.
7. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Cresol causes severe burns [1]. It may be fatal if absorbed through skin, inhaled or ingested. All work with it should be performed in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 5 to 20 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front sorbent section (together with the front glass wool plug) and back sorbent sections of the sampler tube in separate vials. Discard the foam plug.
6. Add 1.0 mL acetone to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.02 to 1.2 mg cresols per sample.
   a. Add known amounts of calibration stock solution to acetone in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (total peak area vs. mg cresols).
9. Determine desorption efficiency (DE) at least once for each batch of silica gel used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg cresols recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2001-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with acetone, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure total peak area of the two cresol peaks.
    NOTE: m-Cresol and p-cresol have the same retention time.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of cresols found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of cresols in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

The precision and bias were determined by sampling and analyzing generated atmospheres containing 10.5 , 21.0, and 42.2 mg/m^3 at 22 °C and 760 mm Hg using 20-L samples. These concentrations were determined from the delivery rate of the syringe drive pump and the flow rates of the dilution air. The stability of the concentrations was monitored with a total hydrocarbon analyzer. Breakthrough of the front section of the silica gel tube was not observed after sampling 44 L of dry test atmosphere containing 42.2 mg/m^3 for 240 min at 0.185 L/min. The isomers of cresol at the 22 mg/m^3 level were stable on silica gel for at least one week. Desorption efficiencies were $\geq$ 0.98. More specific information is given in reference [2].

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Cresol, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-133 (1978).
[2] Documentation of the NIOSH Validation Tests, S167, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3, S167, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[4] "Physical Properties of Chemical Compounds," Advances in Chemistry Series, No. 15, ACS (1955).

METHOD REVISED BY: Julie R. Okenfuss, NIOSH/DPSE; S167 originally validated under NIOSH Contract CDC-99-74-45.

Table 1. Physical properties [4].

Compound	BP (°C)	Density @ 20 °C	Vapor Pressure @ 25 °C (kPa)	Vapor Pressure @ 25 °C (mm Hg)
o-cresol	190.9	1.047 g/mL	57	0.43
m-cresol	202.2	1.034	26	0.19
p-cresol	201.9	1.034	26	0.20

FORMULA: HCN and salts

M.W.: 27.03 (HCN); 65.11 (KCN)

CYANIDES, aerosol and gas

METHOD: 7904
ISSUED: 2/15/84

OSHA: 11 mg/m³; skin (HCN)
5 mg/m³; skin (cyanides, as CN^-)
NIOSH: 5 mg/m³/10 min (as CN^-) [1]
ACGIH: C 10 mg/m³; skin (HCN);
5 mg/m³; skin (cyanides, as CN)

PROPERTIES: HCN: gas, BP 26 °C
KCN: solid, d 1.52 g/mL, MP 634 °C

SYNONYMS: HCN: hydrocyanic acid, prussic acid, formonitrile, CAS #74-90-8.
cyanides: CAS #151-50-8; CAS #143-33-9.

SAMPLING

SAMPLER: FILTER + BUBBLER
(0.8-µm cellulose ester membrane
+ 10 mL 0.1 N KOH)

FLOW RATE: 0.5 to 1 L/min

VOL-MIN: 10 L @ 5 mg/m³ (as CN^-)
-MAX: 180 L @ 11 mg/m³ (as CN^-)

SHIPMENT: routine

SAMPLE STABILITY: HCN stable in 0.1 N KOH at least 1 week [1]; particulate on filter may liberate HCN gas [2]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 5 to 21 mg/m³ (HCN) [3];
2.6 to 10 mg/m³ (KCN) [2]

BIAS: not significant [2,3]

OVERALL PRECISION (s_r): 0.081 (HCN) [3];
0.103 (KCN) [2]

MEASUREMENT

TECHNIQUE: ION-SPECIFIC ELECTRODE

ANALYTE: cyanide ion (CN^-)

EXTRACT FILTER: 25 mL 0.1 N KOH; 30 min

RINSE BUBBLER: 2 mL 0.1 N KOH; dilute to 25 mL with 0.1 N KOH

MEASURE: mV reading of cyanide ion electrode vs. reference electrode

CALIBRATION: solutions of KCN in 0.1 N KOH

RANGE: 0.05 to 2 mg CN^-

ESTIMATED LOD: 2.5 µg CN^- [2]

PRECISION (s_r): 0.043 (HCN) [3];
0.038 (KCN) [2]

APPLICABILITY: The working range (as CN^-) is 0.5 to 15 mg/m³ for a 90-L air sample or 5 to 20 mg/m³ for a 10-L air sample.

INTERFERENCES: Sulfide, chloride, iodide, bromide, cadmium, zinc, silver, nickel, cuprous iron and mercury interfere. In humid atmospheres, some particulate cyanide collected on the filter will liberate hydrogen cyanide which will be trapped in the bubbler [2]. The method cannot distinguish between HCN formed in this manner and HCN originally present in air.

OTHER METHODS: This method combines and replaces Methods S288 [4], S250 [5], and P&CAM 116 [6].

REAGENTS:

1. Double distilled (d.d.) water.
2. Potassium cyanide.*
3. Calibration stock solution, 1000 µg CN^-/mL. Dissolve 0.250 g KCN in 0.1 N KOH to make 100 mL solution. Stable for at least 1 week in polyethylene bottle.
4. Potassium hydroxide (KOH), 0.1 N. Dissolve 5.6 g KOH in d.d water; dilute to 1000 mL.
5. Lead acetate paper.
6. Cadmium carbonate (if sulfide present).
7. Hydrogen peroxide, 30% (if sulfide present).
8. Sodium sulfite, 1 M (if sulfide present).

*See Special Precautions.

EQUIPMENT:

1. Sampler: mixed cellulose ester membrane filter, 37-mm diameter, 0.8-µm pore size, followed by a glass midget bubbler containing 15 mL 0.1 N KOH.
2. Personal sampling pump, 0.5 to 1 L/min, with splashover protection and flexible connecting tubing.
3. Vials, polyethylene, with screw caps, 20-mL, and plastic tape for sealing.
4. Cyanide ion electrode, (Orion 94-06 or equivalent).
5. Reference electrode.
6. pH meter, readable to 0.1 mV.
7. Magnetic stirrer and stirring bars.
8. Jars, ointment, 60-mL, squat-form with aluminum-lined screw caps.
9. Pipets, 0.05- to 2- and 25-mL, with pipet bulb.
10. Volumetric flasks, 25-mL.
11. Beakers, 50-mL.
12. Analytical balance, readable to 0.1 mg.

SPECIAL PRECAUTIONS: Hydrogen cyanide gas and the cyanide particulates may be fatal if swallowed, inhaled or absorbed through the skin. Work in a hood.

Amyl nitrite is the antidote for cyanide poisoning [1].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at 0.5 to 1 L/min for a total sample size of 10 to 180 L.
   NOTE: Maintain bubblers in a vertical position during sampling. Do not allow the solution level to fall below 10 mL.
3. Remove the bubbler stem and tap it gently against the inside wall of the bubbler. Rinse the bubbler stem with 1 to 2 mL of unused 0.1 N KOH. Add the rinse to the bubbler.
4. Quantitatively transfer the contents of the bubbler to a 20-mL vial. Close cap tightly and wrap with plastic tape to avoid sample loss during transit. Label each vial.

SAMPLE PREPARATION:

5. Transfer the filter from the cassette filter holder to a 60-mL ointment jar.
6. Pipet 25.0 mL 0.1 N KOH into the jar. Cap and allow to stand for at least 30 min with occasional shaking to complete extraction. Analyze within 2 hrs after extraction.
7. Empty the contents of the vial into a 25-mL volumetric flask using 0.1 N KOH to rinse the vial. Add rinse to the volumetric flask. Dilute to the mark with 0.1 N KOH.
   NOTE: Sulfide ion irreversibly poisons the cyanide ion specific electrode and must be removed if present. Check for the presence of sulfide ion by touching a drop of sample to a piece of lead acetate paper; the paper will discolor in the presence of sulfide ion. If this test is positive, remove sulfide by one of the following methods:

   a. Add 1 mL 1 M H_2O_2 and 1 mL 1 M Na_2SO_3 to sample solutions prior to diluting to volume; or

b. Add a small amount (spatula tip) of powdered cadmium carbonate to the sample. Swirl to disperse the solid and recheck the liquid with lead acetate paper. If sulfide ion has not been removed completely, add more cadmium carbonate. Avoid a large excess of cadmium carbonate and long contact time with the solution. When a drop of liquid no longer discolors a strip of lead acetate paper, filter the sample through a small plug of glass wool in a Pasteur pipette and proceed with the analysis.

CALIBRATION AND QUALITY CONTROL:

8. Prepare at least five working standards fresh daily to cover the range 50 to 2000 µg CN^- per sample by diluting aliquots of 1000 µg/mL calibration stock solution with 0.1 N KOH (e.g., 0.05 to 2.0 mL calibration stock solution diluted to 25 mL).
9. Analyze the working standards according to steps 11 and 12 together with the samples and blanks.
10. Prepare a calibration graph on semilog paper by plotting cyanide ion concentration on the logarithmic axis and mV on the linear axis.

MEASUREMENT:

11. Transfer the solution to be measured to a 50-mL beaker. Immerse the cyanide ion electrode and reference electrode in the sample and start the magnetic stirrer.
12. With the magnetic stirrer on, allow the potential reading to stabilize. Record the mV reading.

NOTE 1: Potential readings are a function of temperature. Measure samples and working standards at the same temperature (± 2 °C).

NOTE 2: The cyanide electrode will malfunction if chloride, iodide and bromide ions, which form insoluble silver salts, are present in sufficient quantity. Several metal ions are also known to complex with cyanide such as cadmium, zinc, silver, nickel, cuprous iron and mercury. Consult the electrode instruction manual for the procedure to use when such ions are present.

CALCULATIONS:

13. Read the mass, µg, of cyanide ion present in the sample filter (W_f), sample bubbler (W_b), average media blank filter (B_f) and media blank bubblers (B_b) from the calibration graph.
14. Calculate the concentration (mg/m^3) of particulate cyanide, Cp, and hydrogen cyanide, C_{HCN}, in the air volume sampled, V (L):

$$Cp = \frac{W_f - B_f}{V}, \ mg/m^3 \text{ and } C_{HCN} = \frac{(W_b - B_b) \cdot 1.04}{V}, \ mg/m^3$$

where 1.04 is the stoichiometric conversion factor from CN^- to HCN.

NOTE: Particulate cyanides will be collected on the filter. In humid atmospheres, however, it has been observed that during the collection of particulate cyanide, HCN is gradually liberated [2]; therefore, particulate cyanide interference is not completely removed.

EVALUATION OF METHOD:

HCN: Method S288 was issued on September 2, 1977 [4]. Test atmospheres of HCN were generated by calibrated flow from a compressed mixture of HCN in nitrogen [3,7]. The range of HCN concentrations in air was 5 to 21 mg/m^3 for 12-L air samples. Eighteen HCN samples collected at 0.2 L/min for 60 min indicated overall precision of 6.2%, with a 96.7% recovery. An eight-day storage stability study involving six samples at the OSHA standard concentration

level indicated a 92.4% average recovery for the one-day old samples and a 92.6% for eight-day old samples. A collection efficiency study at twice the OSHA standard level, which included backup bubblers, indicated that an average of 99.8% of HCN was collected in the first bubbler. The HCN air generated concentrations were independently confirmed by a titration method [3].

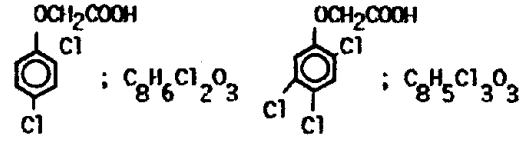
KCN: Method S250 was issued on January 30, 1976 [5]. A set of six weighed KCN samples in the range of 1.8 to 2.5 mg KCN per filter indicated a 97% recovery and a 3.8% measurement precision [2]. Spiking with aqueous or basic solutions of KCN proved unsuccessful (low recovery) because of the cyanide instability in the presence of water and CO_2. Test atmospheres of KCN were generated by atomization of an aqueous solution (162 g/L) of KCN into a dry airstream. Eighteen KCN samples collected in 0.1 N NaOH at 1.5 L/min for 60 min indicated overall precision, s_r, of 0.09. Collection was accomplished with cellulose ester membrane filters followed with backup bubblers. The collection efficiency at twice the OSHA level was 100.0% on the filters. Cyanide salts are known to decompose in moist air with liberation of HCN. This instabilty was determined with two sets of six samples at the one and two times the OSHA level. Each of the samples which were twice the OSHA level were connected with two backup bubblers. Both sets indicated a loss of 16.5%.

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Hydrogen Cyanide and Cyanide Salts, 5-9, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-108 (1976).
[2] Documentation of the NIOSH Validation Tests, S250, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[3] Backup Data Report for Hydrogen Cyanide, S288, available as "Ten NIOSH Analytical Methods, Set 5," Order No. BP 287-499 from NTIS, Springfield, VA 22161.
[4] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, S288, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[5] Ibid, V. 3, S250, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[6] Ibid, V. 1, P&CAM 116, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[7] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY: J. Palassis, NIOSH/DPSE; S250 and S288 originally validated under NIOSH Contracts CDC-99-74-45 and 210-76-0123, respectively.

2,4—D AND 2,4,5—T

FORMULA:  ; $C_8H_6Cl_2O_3$; $C_8H_5Cl_3O_3$

	2,4-D	2,4,5-T
M.W.:	221.04	255.49

METHOD: 5001
ISSUED: 2/15/84

OSHA: 10 mg/m³ (2,4-D or 2,4,5-T)
NIOSH: Group I, II and II Pesticides [1]
ACGIH: 10 mg/m³, STEL 20 mg/m³

PROPERTIES: solid;
MP 153 °C (2,4,5-T); MP 138 °C (2,4-D);
VP not significant

SYNONYMS: 2,4-D: (2,4-dichlorophenoxy)acetic acid; CAS #94-75-7.
2,4,5-T: (2,4,5-trichlorophenoxy)acetic acid; CAS #93-76-5.

SAMPLING

SAMPLER: FILTER
(glass fiber, binderless)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 15 L @ 10 mg/m³
-MAX: 200 L

SHIPMENT: routine

SAMPLE STABILITY: at least 1 week @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 5 to 20 mg/m³ [2,3]
(100-L samples)

BIAS: not significant [2,3]

OVERALL PRECISION (s_r): 0.051 (2,4-D) [2];
0.053 (2,4,5-T) [3]

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: 2,4-D or 2,4,5-T anion

DESORPTION: 15 mL CH_3OH; stand 30 min

INJECTION VOLUME: 50 µL

ELUENT: 0.001 M $NaClO_4$-0.001 M $Na_2B_4O_7$ (2,4-D)
0.003 M $NaClO_4$-0.001 M $Na_2B_4O_7$ (2,4,5-T)

FLOW RATE: 1.7 mL/min

DETECTOR: UV @ 289 nm (2,4,5-T); 284 nm (2,4,-D)

COLUMN: stainless steel, 50 cm x 2 mm ID, packed with Zipax SAX (DuPont); ambient temperature; 6900 kPa (1000 psi)

CALIBRATION: solutions of analyte in methanol

RANGE: 0.15 to 2 mg per filter

ESTIMATED LOD: 0.015 mg per filter (2,4-D) [2];
0.030 mg per filter (2,4,5-T) [3]

PRECISION (s_r): 0.01 (2,4-D) [2];
0.025 (2,4,5-T) [3]

APPLICABILITY: The working range is 1.5 to 20 mg/m³ of either compound for a 100-L air sample. This method determines 2,4-D, 2,4,5-T, and their salts, but not their esters.

INTERFERENCES: High concentrations of esters of either compound do not interfere but require the use of a precolumn to prevent degradation of the HPLC column.

OTHER METHODS: This method combines and replaces Methods S279 [4] and S303 [4] which are the same except for eluent composition and UV detector wavelength.

REAGENTS:

1. 2,4-dichlorophenoxyacetic acid.*
2. 2,4,5-trichlorophenoxyacetic acid.*
3. Methanol, HPLC grade.
4. LC eluent:
   a. 2,4-D: 0.001 M $NaClO_4$ and 0.001 M $Na_2B_4O_7$. Add 0.122 g $NaClO_4$ and 0.381 g $Na_2B_4O_7 \cdot 10H_2O$ to a 1-L volumetric flask. Bring to volume with distilled water. Mix, filter and degas the solution.
   b. 2,4,5-T: 0.003 M $NaClO_4$ and 0.001 M $Na_2B_4O_7 \cdot 10H_2O$. Add 0.366 g $NaClO_4$ and 0.381 g $Na_2B_4O_7 \cdot 10H_2O$ to a 1-L volumetric flask. Bring to volume with distilled water. Mix, filter and degas the solution.
5. Compressed, filtered air or nitrogen for drying syringes.
6. Ethanol, absolute.
7. Acetone.
8. Calibration stock solution, 400 µg/mL. Dissolve 0.400 g 2,4-D or 2,4,5-T in methanol and dilute to 1 L with methanol.
9. Recovery stock solution:
   a. Dissolve 0.248 g 2,4-D in ethanol. Dilute to 10 mL with ethanol.
   b. Dissolve 0.250 g 2,4,5-T, triethylamine salt, in acetone (or 0.250 g 2,4,5-T in methanol). Dilute to 10 mL with acetone.

   NOTE: Use the same form (e.g., acid or salt) of 2,4,5-T as in the air sample. Recovery may vary with the chemical form.

   *See special precautions.

EQUIPMENT:

1. Sampler: filter, glass fiber, binderless, in a 37-mm polystyrene two-piece cassette filter holder (Gelman type AE or equivalent).
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. High pressure liquid chromatograph, UV detector at 284 nm (2,4-D) and 289 nm (2,4,5-T), integrator and column (page 5001-1).
4. Filter, PTFE, 5-µm, 13-mm diameter in Swinny stainless (13-mm) filter holder.
5. Tweezers.
6. Syringes, 20-mL luer-lock.*
7. Vials, glass, 20-mL.*
8. Volumetric flasks, convenient sizes for preparing standard solutions.*

*Wash all glassware with detergent, thoroughly rinse with tap water and distilled water.

SPECIAL PRECAUTIONS: 2,4-D and 2,4,5-T are suspected animal carcinogens [1]. 2,3,7,8-Tetrachlorodibenzo-1,4-dioxin has been identified as an impurity in 2,4,5-T. Avoid any contact with these substances.

SAMPLING:

1. Calibrate each personal sampling pump with a representative filter in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 15 to 200 L. Do not exceed a total dust loading of 2 mg on the filter.
3. Obtain information on the chemical form of the analyte (i.e., ester, salt or free acid) likely to be present in the air sample.

SAMPLE PREPARATION:

4. Remove the filter from the cassette with clean tweezers and place it in a 20-mL vial.
5. Add 15 mL methanol and mix by swirling. Allow to stand at least 30 min.
6. Filter the sample.
   a. Pour the sample solution into a 20-mL syringe which is fitted with a 5-µm PTFE filter.
   b. Filter the sample into a clean vial.
   c. Clean the PTFE filter by backflushing with methanol. Rinse the syringe and plunger with methanol. Dry with air or nitrogen.

CALIBRATION AND QUALITY CONTROL:

7. Calibrate daily with at least five working standards.
   a. Dilute aliquots of calibration stock solution to 10 mL with methanol in volumetric flasks.
   b. Analyze working standards (steps 9 and 10).
   c. Prepare calibration graph (peak area vs. mg 2,4-D or mg 2,4,5-T).
8. Check recovery with at least four spiked media blanks at each of four levels.
   a. Add aliquot of recovery stock solution to media blank.
   b. Analyze using standards prepared from the recovery stock solution.
   c. Calculate R (mg recovered/mg added).

MEASUREMENT:

9. Establish chromatographic conditions listed on page 5001-1 for either 2,4-D or 2,4,5-T.
10. Inject 50 µL of sample in duplicate. Rinse and dry the syringe between samples.
    NOTE 1: The analyte is the chlorinated phenoxyacetate, whether the air sample contained salts or free acid forms of 2,4-D and 2,4,5-T.
    NOTE 2: Esters of 2,4-D and 2,4,5-T will not elute from the HPLC column and may, if present in large amounts, degrade the HPLC column. Protect the main column with a precolumn of Zipax SAX if esters are known to be present. The sample preparation conditions are sufficiently mild so as to preclude hydrolysis of the esters.

CALCULATIONS:

11. Read the mass of analyte, mg (corrected for recovery), in the sample (W) and average media blank (B) from the calibration curve.
12. Calculate the concentration, C (mg/m^3), of 2,4-D or 2,4,5-T in air volume, V (L), taken:

$$C = \frac{(W - B) \cdot 10^3}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Methods S279 (2,4-D) and S303 (2,4,5-T) were issued on February 17, 1978, and March 17, 1978, respectively [4], and validated using 100-L air samples [2,3,5]. Atmospheres were generated using 2,4-D dimethylamine salt for S279 and Weedar Amine BK (Amchem; equal parts of 2,4-D dimethylamine salt and 2,4,5-T triethylamine salt) for S303. Overall precision and recovery for 100-L samples were as shown, representing non-significant bias in each method:

Method	Overall Precision (s_r)	Range Studied		Recovery @ 0.5 mg	7-Day Storage Stability, % of Day 1
		mg/m³	mg per sample		
S279	0.051	5 to 20	0.5 to 2	0.97	99
S303	0.053	5 to 21	0.5 to 2	0.86 to 0.99	104

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure During Manufactur and Formulation of Pesticides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-174 (1978).

[2] Backup Data Report S279 for 2,4-D prepared under NIOSH Contract No. 210-76-0123 (unpublished, 1976), available as "Ten NIOSH Analytical Methods, Set 6," Order No. PB 288-629 from NTIS, Springfield, VA 22161.

[3] Backup Data Report S303 for 2,4,5-T prepared under NIOSH Contract No. 210-76-0123 (unpublished, 1976), available as "Ten NIOSH Analytical Methods, Set 6," Order No. PB 288-629 from NTIS, Springfield, VA 22161.

[4] NIOSH Manual of Analytical Methods, 2nd ed., V. 5, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).

[5] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY: Robert W. Kurimo, NIOSH/DPSE; originally validated under NIOSH Contract No. 210-76-0123.

FORMULA: $(ClCH_2CH_2)_2O$; $C_4H_8Cl_2O$

M.W.: 143.01

sym—DICHLOROETHYL ETHER

METHOD: 1004
ISSUED: 2/15/84

OSHA: C 15 ppm (87.7 mg/m³)
NIOSH: no standard
ACGIH: 5 ppm (skin); STEL 10 ppm
(1 ppm = 5.85 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.218 g/mL @ 20 °C;
BP 178 °C; MP -50 °C;
VP 50 Pa (0.4 mm Hg; 530 ppm) @ 20 °C

SYNONYMS: bis(2-chloroethyl)ether; 1,1'-oxybis[2-chloroethane]; CAS #111-44-4.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 1 L/min

VOL-MIN: 2 L @ 15 ppm
-MAX: 15 L

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days @ 25 °C [2]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 45 to 180 mg/m³ [2]
(15-L samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.059 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: sym-dichloroethyl ether

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 200 - 225 °C
-DETECTOR: 250 - 275 °C
-COLUMN: 100 - 135 °C

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: 3 m x 3 mm ID stainless steel; 10% FFAP on 80/100 mesh DMCS Chromosorb W-AW or equivalent

CALIBRATION: sym-dichloroethyl ether in CS_2

RANGE: 0.15 to 4 mg per sample [1]

ESTIMATED LOD: 0.01 mg per sample [3]

PRECISION (s_r): 0.007 [2]

APPLICABILITY: The working range is 10 to 270 mg/m³ for a 15-L air sample. This method may be used for simultaneous analysis of two or more analytes by changing the chromatographic conditions (e.g., temperature programming). High humidity during sampling will greatly reduce breakthrough volume.

INTERFERENCES: None identified. Alternate columns, e.g., 10% SP-1000 on 80/100 mesh Supelcoport, SP-2100 with 0.1% Carbowax 1500 or DB-1 fused silica capillary column may be used.

OTHER METHODS: This is Method S357 [1] in a revised format.

REAGENTS:

1. Eluent: Carbon disulfide*, chromatographic quality containing 0.1% (v/v) toluene or other suitable internal standard.
2. sym-Dichloroethyl ether (DCEE).
3. Hexane.
4. Calibration stock solution, 0.244 mg/µL. Dilute 2.44 g DCEE (2.0 mL at 20 °C) to 10 mL with hexane. Prepare in duplicate.
5. Nitrogen, purified.
6. Hydrogen, prepurified.
7. Air, filtered.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 1004-1).
4. Vials, 2-mL, PTFE-lined caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 1 L/min for a total sample size of 2 to 15 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.01 to 4 mg DCEE per sample.
   a. Add known amounts of calibration stock solution to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg DCEE).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.

c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg DCEE recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1004-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of DCEE found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of DCEE in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S357 [1] was issued on May 21, 1976, and validated over the range 45 to 180 mg/m³ at 24 °C and 762 mm Hg using a 15-L sample [2]. Overall precision, s_r, was 0.059 with average recovery 90.7%, representing a non-significant bias. The concentration of DCEE was independently verified by a direct hydrocarbon analyzer. Desorption efficiency was 0.94 in the range 0.7 mg to 2.7 mg per sample. Breakthrough (5% on back section) occurred at 115 min when sampling an atmosphere containing 161 mg/m³ at 0.9 L/min in dry air.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd ed., V. 3, S357, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[2] Documentation of the NIOSH Validation Tests, NIOSH, S357-1, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[3] User check, UBTL, NIOSH Sequence #4121-J (unpublished, November 21, 1983).

METHOD REVISED BY: G. David Foley, Y. T. Gagnon, and K. J. Williams, NIOSH/DPSE; S357 originally validated under NIOSH Contract CDC-99-74-45.

FORMULA: $H_3CC(Cl)_2NO_2$;
$C_2H_3Cl_2NO_2$

M.W.: 143.96

1,1—DICHLORO—1—NITROETHANE

METHOD: 1601
ISSUED: 2/15/84

OSHA: C 10 ppm
NIOSH: no standard
ACGIH: 2 ppm; STEL 10 ppm
(1 ppm = 5.89 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.405 g/mL @ 20 °C;
BP 124 °C;
VP 2 kPa (15 mm Hg; 2% v/v) @ 20 °C

SYNONYMS: CAS #594-72-9.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(petroleum charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 1 L/min

VOL-MIN: 1 L @ 10 ppm
-MAX: 15 L

SHIPMENT: routine

SAMPLE STABILITY: at least 5 days @ 25 °C [2]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 27 to 115 mg/m³ [2]
(17-L samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.055 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: 1,1-dichloro-1-nitroethane

DESORPTION: 1 mL CS_2, stand 30 min

TEMPERATURE-INJECTION: 225 °C
-DETECTOR: 250 °C
-COLUMN: 70 °C

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: 3 m x 3 mm stainless steel, 5% SP-1000 on 100/120 mesh Chromosorb WHP, or equivalent

CALIBRATION: analyte solutions in CS_2 with undecane as internal standard

RANGE: 0.09 to 2.7 mg per sample [1]

ESTIMATED LOD: 0.01 mg per sample

PRECISION (s_r): 0.038 [2]

APPLICABILITY: The working range is 6 to 180 mg/m³ for a 15-L air sample. The method is applicable to ceiling determinations.

INTERFERENCES: None identified. Alternate chromatographic columns to circumvent interferences are SP-2100, SP-2100 with 0.1% Carbowax 1500 or DB-1 fused silica capillary column.

OTHER METHODS: This is Method S213 [1] in a revised format.

Preceding page blank

REAGENTS:

1. Eluent: Carbon disulfide,* chromatographic quality, containing 0.2% v/v undecane or other suitable internal standard.
2. 1,1-Dichloro-1-nitroethane.
3. Calibration stock solution, 0.211 mg/µL. Dilute 2.11 g 1,1-dichloro-1-nitroethane (1.5 mL @ 20 °C) to 10 mL with CS_2. Prepare in duplicate.
4. Nitrogen, purified.
5. Hydrogen, prepurified.
6. Air.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing two sections of 20/40 mesh activated petroleum-based charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available (e.g., SKC Lot 104).
2. Personal sampling pump, 0.01 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 1601-1).
4. Vials, 2-mL, PTFE-lined caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 1 L/min for a total sample size of 1 to 15 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.01 to 2.7 mg 1,1-dichloro-1-nitroethane per sample.
   a. Add known amounts of calibration stock solution to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg 1,1-dichloro-1-nitroethane).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.

c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg 1,1-dichloro-1-nitroethane recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1601-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of 1,1-dichloro-1-nitroethane found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of 1,1-dichloro-1-nitroethane in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S213 [1] was issued on November 21, 1975, and validated over the range 27 to 115 mg/m^3 at 23 °C and 763 mm Hg using a 17-L sample [2]. Overall precision, s_r, was 0.055, with average recovery 97.7%, representing a non-significant bias. SKC Lot 104 charcoal was the collecting medium. The concentration of analyte was independently verified by calibrated syringe pump. Desorption efficiency was 0.910 in the range 0.5 mg to 2.0 mg analyte per sample. Breakthrough (5% on back section) occurred at 193 min when sampling an atmosphere containing 116 mg/m^3 1,1-dichloro-1-nitroethane at 0.79 L/min in dry air.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd ed., V. 3, S213, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[2] Documentation of the NIOSH Validation Tests, NIOSH, S213, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).

METHOD REVISED BY: G. David Foley, Y. T. Gagnon, and K. J. Williams, NIOSH/DPSE; S213 originally validated under NIOSH Contract CDC-99-74-45.

FORMULA: Table 1

DYES, BENZIDINE-, o—TOLIDINE—, o—DIANISIDINE

METHOD: 5013
ISSUED: 2/15/84

M.W.: Table 1

OSHA: no standard
NIOSH: lowest feasible level [1,2]
ACGIH: no standard

PROPERTIES: colored powders; water soluble; VP not significant

SYNONYMS: Table 1.

SAMPLING

SAMPLER: FILTER
(5-µm PTFE membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 120 L
-MAX: 500 L

SHIPMENT: keep samples dry and cool; protect from light

SAMPLE STABILITY: at least 7 days @ 25 °C in the dark

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: include 1 bulk sample for each dye present on the filter

ACCURACY

RANGE STUDIED: not studied

BIAS: none identified

OVERALL PRECISION (s_r): not evaluated

MEASUREMENT

TECHNIQUE: HPLC, UV

ANALYTE: benzidine, o-tolidine, o-dianisidine

DESORPTION: H_2O, 2 mL

REDUCTION: reductive cleavage of dye to free amine with sodium hydrosulfite in aqueous phosphate buffer

INJECTION VOLUME: 10 µL

COLUMN: Waters Radial Pak C_{18} with Radial Compression Module or equivalent

DETECTOR: UV detector set @ 280 nm

MOBILE PHASE: 60% methanol/40% phosphate buffer

CALIBRATION: solutions of benzidine, o-tolidine and o-dianisidine in methanol

RANGE: ca. 15 to 250 µg per sample (Table 1)

ESTIMATED LOD: not determined

PRECISION (s_r): 0.04 to 0.08 [3,4]

APPLICABILITY: The working range is ca. 0.06 to 1 mg/m³ for a 250-L air sample. This method determines benzidine, o-tolidine or o-dianisidine from dyes based on these aromatic amines, but will not distinguish between different dyes based on the same amine moiety. The method will not distinguish between benzidine obtained from reduction of the dyes and free benzidine in the dye formulation.

INTERFERENCES: Aniline, azobenzene, p-aminophenol, p-phenylenediamine or p-nitroaniline do not interfere in the measurement when present in equimolar amounts.

OTHER METHODS: This is P&CAM 325 [3,4] in a revised format. P&CAM 234 [1,5], a general colorimetric method for diazonium salts and azo dyes, has not been revised.

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REAGENTS:

1. Water, deionized and distilled.
2. Methanol, HPLC Grade.
3. Benzidine.*
4. o-Tolidine.*
5. o-Dianisidine.*
6. Calibration stock solutions. Dilute the following amounts to 10 mL with methanol. Stable one month at 4 °C.
   a. Benzidine, 15.6 mg
   b. o-Tolidine, 15.3 mg
   c. o-Dianisidine, 5.6 mg
7. Disodium hydrogen phosphate, Na_2HPO_4.
8. Potassium dihydrogen phosphate, KH_2PO_4.
9. Sodium hydrosulfite, $Na_2S_2O_4$.
10. HPLC mobile phase buffer. Dilute 3.39 g KH_2PO_4 and 4.30 g Na_2HPO_4 to 1 L with water. Prepare daily.
11. Reduction buffer.
    a. Solution A. Dilute 1.179 g KH_2PO_4 to 1 L with water. Prepare daily.
    b. Solution B. Dilute 11.79 g KH_2PO_4 and 43.00 g Na_2HPO_4 to 1 L with water. Prepare daily.
12. Reducing solution. Dilute 100 mg $Na_2S_2O_4$ to 10 mL with the appropriate reduction buffer of solution A or B (See Table 1) immediately before use.

*See Special Precautions.

EQUIPMENT:

1. Sampler: PTFE filter, 5-µm, 37-mm, (Millipore Mitex or equivalent) with backup pad in a three-piece plastic cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. High pressure liquid chromatograph equipped with 280-nm UV detector, integrator and column (page 5013-1), Waters Model RCM 100 Radial Compression Module with Waters Radial Pak C_{18} column or equivalent.
4. Syringe or autosampler for HPLC injection.
5. Syringes, volumetric, 10-, 25- and 50-µL.
6. Flasks, volumetric, 10- and 100-mL, 1-L.
7. Vials, 4-mL, with screw caps.
8. Pipettes, volumetric, 1-mL.
9. Tweezers.
10. Beakers, 50-mL.
11. Ultrasonic water bath.

SPECIAL PRECAUTIONS: NIOSH recommends that benzidine- and benzidine-congener-based dyes be recognized and handled as human carcinogens because they can be reduced to the free aromatic amine in living systems and eliminated by the usual metabolic pathways [1,2].

Benzidine is a recognized human carcinogen and regulated by the Occupational Safety and Health Administration. o-Tolidine and o-dianisidine are currently suspect carcinogens and should be handled accordingly [1,2]

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 120 to 500 L.

SAMPLE PREPARATION:

3. Remove the filter from the cassette with clean tweezers and place it face up in a 50-mL beaker.
4. Add 1.0 mL of water to the beaker and swirl to wet the entire deposit.
5. Add a second 1.0-mL of water to the beaker and shake.
6. Turn the filter sample side down and place the beaker in an ultrasonic bath for 15 min.
7. Pipette 1.0 mL of the sample solution to a 4-mL vial.
8. Add 1.0 mL of freshly prepared reducing solution.
   NOTE: Where the composition of the sample dye is unknown or different from the dyes listed in Table 1, reduce a 1-mL aliquot of the desorbed dye solution with the reducing solution made from buffer A. If precipitation of the dye from solution is observed at this point, reduce the remaining 1-mL aliquot of the desorbed dye solution with the reduction solution made with buffer B.
9. Cap the vial and allow to stand with occasional shaking for at least 1 hr or until the change in solution color is completed.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily.
    a. Dilute aliquots of the calibration stock solutions for each of the amines (benzidine, o-tolidine, o-dianisidine) to 10 mL with methanol in volumetric flasks. Prepare at least five working standards to cover the ranges of interest (0.38 to 16 µg/mL benzidine; 0.77 to 15.3 µg/mL, o-tolidine; 0.56 to 11.7 µg/mL o-dianisidine).
    b. Analyze the working standards together with samples and blanks (steps 12 through 14).
    c. Prepare separate calibration graphs (peak area vs. µg per sample) for benzidine, o-tolidine and o-dianisidine. At the completion of step 9, the total effective volume of the solution containing the entire sample is 4 mL.
11. Determine recovery if the filter sample is known to contain only one dye.
    a. Prepare a solution of a known concentration of the bulk sample of the dye in 10 mL H_2O.
    b. Add known volumes of this solution to PTFE filters using a microliter syringe and allow to dry. Prepare three filters at each of five concentration levels.
    c. Analyze the filters by steps 3 through 9 and 12 through 14.
    d. On the day of analysis of the filters, add the same volume of dye solution which was spiked onto the filters to 2.0 mL H_2O.
    e. Calculate recovery (µg benzidine, o-tolidine or o-dianisidine recovered from the filter/µg from step 11.d).
    f. Prepare graph of recovery vs. µg benzidine, o-tolidine or o-dianisidine recovered.

MEASUREMENT:

12. Set the HPLC to conditions given on page 5013-1.
13. Inject 10 µL sample into the HPLC. Make duplicate injections of samples and standards.
14. Measure peak areas.

CALCULATIONS:

15. Read the mass, µg (corrected for recovery if applicable) of the free amine corresponding to each peak area for the sample (W) and average media blank (B) from the appropriate calibration graph.
16. Calculate the concentration, C, of benzidine, o-tolidine or o-dianisidine in the air volume sampled, V (L):

$$C = \frac{(W - B)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was laboratory evaluated over the ranges listed in Table 1 [3]. The concentration of dye remaining after reduction varied from 0 to 6% as determined by visible spectrophotometry. The reduced free amine was confirmed by GC/MS. The lower end of the analytical range was defined as the level which gave at least 75% recovery with approximately 10% s_r. For C. I. Direct Red 28, the analytical range covered 27.3 to 273 µg dye per sample. The lower level of this range gave 94.4% recovery (s_r = 6.3%) based on free benzidine for six replicate samples. For the other three dyes the results were as follows: C. I. Direct Blue 6, 15.0 to 300.0 µg dye per sample, 100.3% recovery (s_r = 4.34%); C. I. Direct Brown 95, 24.3 to 243 µg dye per sample, 78.5% recovery (s_r = 6.7%) C. I. Direct Black 38, 12.5 to 250.0 µg dye per sample, 78.1% recovery (s_r = 12.8%). The pooled analytical precisions (s_r) for samples at three concentrations in the analytical range for each dye are as follows: Direct Red 28, 0.045; Direct Blue 6, 0.061; Direct Brown 95, 0.072; Direct Black 38, 0.078. Since the method does not distinguish between various benzidine based dyes, recovery correction factors cannot be applied unless a single known dye is contained on the filter. Recovery and stability studies show a recovery of 85% or better (except for Direct Black 38 at the 12.5 µg per sample level) when samples were analyzed within seven days of sampling. Recovery studies must be performed on the bulks collected with the samples due to variability in sample purity and variety of benzidine-based dyes. Recovery studies on spiked samples stored at 75% relative humidity indicated no change due to humidity in the recoveries or sample stability.

REFERENCES:

[1] Special Occupational Hazard Review for Benzidine-Based Dyes, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 80-109 (1979).

[2] Preventing Health Hazards from Exposure to Benzidine Congener Dyes, U.S. Department of Health and Human Services, Publ. (NIOSH) 83-105 (1983).

[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 6, 325, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).

[4] Kennedy, Eugene R. and Martha J. Seymour. Development of an Analytical Method for Benzidine-Based Dyes, Chemical Hazards in the Workplace Measurement and Control, ACS Symposium Series 149, American Chemical Society, Washington, DC, 21-35 (1981).

[5] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).

[6] NIOSH/NCI Current Intelligence Bulletin 24, Benzidine-Derived Dyes, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-148 (1978).

METHOD WRITTEN BY: Eugene R. Kennedy, Ph.D., Martha J. Seymour and Charles E. Neumeister, NIOSH/DPSE.

Table 1. Benzidine- and benzidine-congener-based dyes.

Color Index Name	C.I. Number	Molecular Formula	MW	Synonyms [1,6]	Range[a] µg per sampler	Range[a] µg/m³	HPLC Flow rate (mL/min)	Reduction Buffer[b]
BENZIDINE-BASED:								
C.I. Direct Red 28	22120	$C_{32}H_{22}N_6S_2O_6Na_2$	696.67	Congo Red; CAS #573-58-0	27.3-273	54.6-546	2	B
C.I. Direct Blue 6	22610	$C_{32}H_{20}N_6S_4O_{14}Na_4$	932	Amidine Blue 2B; CAS #2602-46-2	15.0-300	30.0-600	2	B
C.I. Direct Brown 95	30145	$C_{31}H_{18}N_6O_9Na_2Cu$	759	Chrome Leather Brown: CAS #16071-86-6	24.3-242	48.6-485	2	B
C.I. Direct Black 38	30235	$C_{34}H_{25}N_9S_2O_7Na_2$	781	Amidine Black GA; CAS #1937-37-7	12.5-250	25.0-500	1	A
o-TOLIDINE-BASED:								
C.I. Direct Red 2	23500	$C_{34}H_{26}N_6S_2O_6Na_2$	724.74	Benzopurpurine 4B; CAS #992-59-6	16.7-334	33.4-668	1	A
o-DIANISIDINE-BASED:								
C.I. Direct Blue 8	24140	$C_{34}H_{24}N_4S_2O_{10}Na_2$	758.69	Direct Azurine G; Benzo Azurine G; CAS #2429-71-2	10.2-204	20.4-408	1	A

[a]Air concentrations calculated from analytical results with an air volume of 500 L assumed.
[b]The letters "A" and "B" refer to the reduction buffer solutions described in the REAGENTS section, items 11.a and b.

ELEMENTS (ICP)

METHOD: 7300
ISSUED: 2/15/84

M.W.: Table 1

OSHA/NIOSH/ACGIH: Table 1

PROPERTIES: Table 1

ELEMENTS:	aluminum	cobalt	manganese	silver	tungsten
	arsenic	copper	molybdenum	sodium	vanadium
	beryllium	iron	nickel	tellurium	yttrium
	cadmium	lead	phosphorus	thallium	zinc
	calcium	lithium	platinum	tin	zirconium
	chromium	magnesium	selenium	titanium	

SYNONYMS: vary depending upon the compound.

SAMPLING

SAMPLER: FILTER
(0.8-µm, cellulose ester membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: Table 1
-MAX: Table 1

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: none identified

OVERALL PRECISION (s_r): not evaluated

MEASUREMENT

TECHNIQUE: INDUCTIVELY COUPLED ARGON PLASMA, ATOMIC EMISSION SPECTROSCOPY

ANALYTE: elements above

ASHING REAGENTS: conc. HNO_3, 4 mL;
and conc. $HClO_4$, 1 mL
CONDITIONS: room temperature, 30 min;
150 °C to near dryness

FINAL SOLUTION: 4% HNO_3, 1% $HClO_4$, 10 mL

WAVELENGTH: depends upon element; Table 2

BACKGROUND CORRECTION: spectral wavelength shift

CALIBRATION: elements in 4% HNO_3, 1% $HClO_4$

RANGE: 2.5 to 1000 µg per sample [1]

ESTIMATED LOD: 1 µg per sample [1]

PRECISION (s_r): Table 2

APPLICABILITY: The working range of this method is 0.005 to 2.0 mg/m³ for each element in a 500-L air sample. This is simultaneous elemental analysis, not compound specific. Verify that the types of compounds in the samples are soluble with this ashing procedure.

INTERFERENCES: Spectral interferences are the primary interferences encountered in ICP-AES analysis. These are minimized by judicious wavelength selection, interelement correction factors and background correction [1,2].

OTHER METHODS: This method replaces P&CAM 351 [2] for trace elements. Atomic absorption spectroscopy (e.g., Methods 70XX) is an alternate analytical technique for many of these elements.

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REAGENTS:

1. Nitric acid, conc.
2. Perchloric acid, conc.*
3. Ashing acid: 4:1 (v/v) HNO_3:$HClO_4$. Mix 4 volumes conc. HNO_3 with 1 volume conc. $HClO_4$.
4. Calibration stock solutions, 1000 µg/mL. Commercially available, or prepared per instrument manufacturer's recommendation (see step 12).
5. Dilution acid, 4% HNO_3, 1% $HClO_4$. Add 50 mL ashing acid to 600 mL water; dilute to 1 L.
6. Argon.
7. Distilled,deionized water.

*See Special Precautions.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-µm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Inductively coupled plasma-atomic emission spectrometer, equipped as specified by the manufacturer for analysis of elements of interest.
4. Regulator, two-stage, for argon.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.*
6. Volumetric flasks, 10- and 100- mL.*
7. Assorted volumetric pipets as needed.*
8. Hotplate, surface temperature 150 °C.

*Clean all glassware with conc. nitric acid and rinse thoroughly in distilled water before use.

SPECIAL PRECAUTIONS: Perform all perchloric acid digestions in a perchloric acid hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a total sample size of 200 to 2000 L (see Table 1) for TWA measurements. Do not exceed a filter loading of approximately 2 mg total dust.

SAMPLE PREPARATION:

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
4. Add 5 mL ashing acid. Cover with a watchglass. Let stand 30 min at room temperature.
   NOTE: Start a reagent blank at this step.
5. Heat on hotplate (120 °C) until ca. 0.5 mL remains.
   NOTE: Some species of Li, Mn, Mo, Sn, W, and Zr will not be completely solubilized by this procedure. Alternative solubilization techniques for most of these elements can be found elsewhere [2,3,4,5,6,7].
6. Add 2 mL ashing acid and repeat step 5. Repeat this step until the solution is clear.
7. Remove watchglass and rinse into the beaker with distilled water.
8. Increase the temperature to 150 °C and take the sample to dryness.
9. Dissolve the residue in 2 to 3 mL dilution acid.
10. Transfer the solutions quantitatively to 10-mL volumetric flasks.
11. Dilute to volume with dilution acid.

CALIBRATION AND QUALITY CONTROL:

12. Calibrate the spectrometer according to the manufacturers recommendations.
    NOTE: Typically, an acid blank and 10 µg/mL multielement working standards are used. The following multielement combinations are chemically compatible in 4% HNO_3/1% $HClO_4$:
    a. Ag, Ca, Co, Mn, Pb, V, Zn;
    b. Al, Be, Cd, La, Li, Ni, Tl;
    c. As, B, Ba, Mg, Mo, P, Sn;

d. Cu, Fe, Na, Pt, Sr, Te, Y;
e. Cr, K, Sb, Se, Ti, Zr; and
f. Si, W (distilled water only)

13. Analyze a standard for every ten samples.
14. Check recoveries with at least two spiked media blanks per ten samples.

MEASUREMENT:

15. Set spectrometer to conditions specified by manufacturer.
16. Analyze standards and samples.
    NOTE: If the values for the samples are above the range of the standards, dilute the solutions with dilution acid, reanalyze and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

17. Obtain the solution concentrations for the sample, C_s (µg/mL), and the average media blank, C_b (µg/mL), from the instrument.
18. Using the solution volumes of sample, V_s (mL), and media blank, V_b (mL), calculate the concentration, C (mg/m^3), of each element in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b'}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method P&CAM 351 was evaluated in 1981 [1,2]. The precision and recovery data were determined at 2.5 and 1000 µg of each element per sample on spiked filters. The precision and recovery data, instumental detection limits, sensitivity, and analytical wavelengths are listed in Table 2. The values in Table 2 were determined with a Jarrell-Ash Model 1160 ICP operated according to manufacturer's instructions.

REFERENCES:

[1] Hull, R.D. "Multielement Analysis of Industrial Hygiene Samples," NIOSH Internal Report, presented at the American Industrial Hygiene Conference, Portland, Oregon (May 1981).
[2] NIOSH Manual of Analytical Methods, 2nd ed., V. 7, P&CAM 351, U.S. Department of Health and Human Services, Publ. (NIOSH) 82-100 (1981).
[3] Ibid, S341 (Lead).
[4] Ibid, V. 2, S5 (Manganese), U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[5] Ibid, V. 4, P&CAM 271 (Tungsten), U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[6] Ibid, V. 5, P&CAM 173 (Metals by Atomic Absorption), U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[7] Ibid, V. 3, S183 (Tin), S185 (Zirconium), and S376 (Molybdenum), U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

METHOD REVISED BY: R. DeLon Hull and Mark Millson, NIOSH/DPSE.

Table 1. Properties and sampling volumes.

Element (Symbol)	Properties: Atomic Weight	Properties: MP, °C	Permissible Exposure Limits, mg/m³ TWA OSHA/NIOSH/ACGIH	Air Volume @ OSHA, L: MIN	Air Volume @ OSHA, L: MAX
Silver (Ag)	107.87	961	0.01/ — / 0.1	250	2000
Aluminum (Al)	26.98	660	— / — / 10.	5 (g)	100 (g)
Arsenic (As)	74.92	817*	0.5/C 0.002/ 0.2	5	2000
Beryllium (Be)	9.01	1278	0.002/ 0.0005/ 0.002	1250	2000
Calcium (Ca)	40.08	842	5 (b)/ — / 2 (b)	5	200
Cadmium (Cd)	112.40	321	0.2/ 0.04/ 0.05	13	2000
Cobalt (Co)	58.93	1495	0.1/ — / 0.1	25	2000
Chromium (Cr)	52.00	1890	1.0 (c)/ 0.025/ 0.5 (c)	5	1000
Copper (Cu)	63.54	1083	1.0/ — / 1.0	5	1000
Iron (Fe)	55.85	1535	10 (b)/ — / 5 (b)	5	100
Lithium (Li)	6.94	179	0.025 (d)/ — / 0.025 (d)	100	2000
Magnesium (Mg)	24.31	651	15 (b)/ — / 10 (b)	5	67
Manganese (Mn)	54.94	1244	C 5/ — / C 5	5	200
Molybdenum (Mo)	95.94	651	15 (e)/ — / 10 (e)	5	67
Sodium (Na)	22.99	98	2 (f)/ C 2 (f)/ C 2 (f)	13	2000
Nickel (Ni)	58.71	1453	1/ 0.015/ 1 (c)	5	1000
Phosphorus (P)	30.97	44	— / — / 0.1	25 (g)	2000 (g)
Lead (Pb)	207.19	328	0.05/ 0.1/ 0.15	50	2000
Platinum (Pt)	195.09	1769	0.002 (a)/ — / 1 (c)	1250	2000
Selenium (Se)	78.96	217	0.2/ — / —	13	2000
Tin (Sn)	118.69	232	2/ — / 2 (c)	5	500
Tellurium (Te)	127.60	450	0.1/ — / 0.1	25	2000
Titanium (Ti)	47.90	1675	— / — / 10 (b)	5	100
Thallium (Tl)	204.37	304	0.1 (a)/ — / 0.1 (a)	25	2000
Vanadium (V)	50.94	1890	C 0.5/ 1 (c)/ 0.05 (V_2O_5)	5	2000
Tungsten (W)	183.85	3410	— / 5 (e)/ 5 (e)	5 (g)	200 (g)
Yttrium (Y)	88.91	1495	1/ — / 1	5	1000
Zinc (Zn)	65.37	419	5 (b)/ 5 (b)/ 5 (b)	5	200
Zirconium (Zr)	91.22	1852	5/ — / 5	5	200

(a) soluble
(b) oxide
(c) metal
(d) hydride
(e) insoluble
(f) hydroxide
(g) at the ACGIH TLV

Table 2. Measurement procedures and data (a).

Element	Wavelength (nm)	Instrumental LOD (ng/mL)	Sensitivity (Intensity/ µg/mL)	Recovery (%) @ 2.5 µg/ filter (b)	Recovery (%) @ 1000 µg/ filter	Precision (s_r) (N = 3) @ 2.5 µg/ filter	Precision (s_r) (N = 3) @ 1000 µg/ filter
Ag	328.3	26	0.65	111	91	0.02	0.075
Al	308.2	14	0.23	93	100	0.092	0.023
As	193.7	13	0.57	103	99	0.062	0.026
Be	313.0	1.5	1.29	107	90	0.040	0.034
Ca	315.9	10	0.49	99	95	0.036	0.014
Cd	226.5	1.6	0.83	107	99	0.032	0.020
Co	231.2	7.4	0.38	101	95	0.040	0.005
Cr	205.6	1.3	0.50	98	106	0.053	0.016
Cu	324.8	2.1	0.72	98	99	0.036	0.022
Fe	259.9	3.9	0.13	94	97	0.068	0.016
Li	670.8	2.8	0.48	89	95	0.171	0.043
Mg	279.6	24	0.22	105	106	0.084	0.027
Mn	257.6	0.4	0.74	84	93	0.062	0.035
Mo	281.6	7.0	0.18	94	88	0.023	0.049
Na	589.0	10	0.76	(c)	101	(c)	0.045
Ni	231.6	3.4	0.41	105	97	0.027	0.020
P	214.9	22	0.17	(c)	91	(c)	0.056
Pb	220.4	17	0.42	105	95	0.060	0.011
Pt	203.7	15	0.69	106	91	0.041	0.075
Se	190.6	21	0.28	105	97	0.068	0.049
Sn	190.0	64	0.49	74	67	0.33	0.16
Te	214.3	29	0.41	102	94	0.050	0.063
Ti	334.9	1.2	0.55	96	108	0.051	0.029
Tl	190.9	17	0.22	103	99	0.043	0.017
V	310.2	3.2	0.88	99	94	0.043	0.014
W	207.9	13	2.58	35	23	0.053	0.60
Y	371.0	0.8	2.35	99	100	0.015	0.013
Zn	213.9	0.6	0.60	101	94	0.013	0.013
Zr	339.2	1.9	0.88	75	98	0.049	0.008

(a) Values reported were obtained with a Jarrell-Ash Model 1160 ICP; performance may vary with instrument and should be independently verified.

(b) 2.5 µg/filter corresponds to 5 µg/m^3 for a 500-L air sample.

(c) Blank levels too high to make accurate determinations

FORMULA: CH_2OCHCH_2Cl; C_3H_5OCl

M.W.: 92.53

EPICHLOROHYDRIN

METHOD: 1010
ISSUED: 2/15/84

OSHA: 5 ppm
NIOSH: 2 mg/m³; 19 mg/m³/15 min [1]
ACGIH: 2 ppm (skin); STEL 5 ppm
(1 ppm = 3.78 mg/m³ @ NTP)

PROPERTIES: liquid; d_4^{20} 1.1812; BP 117.9 °C;
MP -25.6 °C;
VP 1.67 kPa (12.5 mm Hg; 16,400 ppm) @ 20 °C;
explosive range 3.8 to 21% v/v in air

SYNONYMS: chloropropylene oxide; 1-chloro-2,3-epoxypropane; chloromethyloxirane; CAS #106-89-8.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min or less

VOL-MIN: 2 L @ 2 ppm
-MAX: 30 L

SHIPMENT: routine

SAMPLE STABILITY: at least 2 weeks @ 25 °C [2]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 12 to 43 mg/m³ [3]
(20-L samples)

BIAS: not significant [3]

OVERALL PRECISION (s_r): 0.057 [3]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: epichlorohydrin

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTOR: 175 °C
-DETECTOR: 215 °C
-COLUMN: 135 °C

CARRIER GAS: N_2 or He, 20 mL/min

COLUMN: 1.8 m x 2 mm ID glass; 80/100 Chromosorb 101 [2]

CALIBRATION: epichlorohydrin in CS_2

RANGE: 0.04 to 1.2 mg per sample [3]

ESTIMATED LOD: 0.001 mg per sample

PRECISION (s_r): 0.031 [3]

APPLICABILITY: The working range is 2 to 60 mg/m³ for a 20-L air sample. A sampling period of 15 min may be monitored for STEL compliance using a flow rate of 0.2 L/min.

INTERFERENCES: None identified.

OTHER METHODS: This is Method S118 in a revised format [4]. A similar method appears in the criteria document [1].

Preceding page blank

REAGENTS:

1. Carbon disulfide, chromatographic quality.*
2. Epichlorohydrin, reagent grade.*
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, filtered.
6. Calibration stock solution, 9.45 mg/mL. Dissolve 80 µL epichlorohydrin in 10 mL CS_2.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing a silylated glass wool plug; a front, 100-mg section of 20/40 mesh activated (600 °C) coconut shell charcoal; a 2-mm urethane foam plug; a rear, 50-mg section of charcoal; and a 3-mm urethane foam plug. Pressure drop across the tube must be less than 3.4 kPa at the sampling flow rate. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible tubing.
3. Gas chromatograph, FID, integrator and column (page 1010-1).
4. Vials, glass, 2-mL, with PTFE-lined caps.
5. Pipet, 1-mL, with pipet bulb.
6. Syringes, 10- and 100-µL.
7. Volumetric flasks, 1- and 10-mL.
8. Metal file.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and extremely flammable (flash point = -30 °C); work with it only in a hood.

Epichlorohydrin is a strong irritant and sensitizer and may cause kidney injury [1].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 2 to 30 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL CS_2 to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.001 to 1.2 mg epichlorohydrin per sample.
   a. Add known amounts of calibration stock solution to CS_2 in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg epichlorohydrin).

9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of epichlorohydrin (or a solution of epichlorohydrin in hexane) directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg epichlorohydrin recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1010-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with CS_2, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of epichlorohydrin found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of epichlorohydrin in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S118 was issued on May 9, 1975 and validated over the range 11.7 to 43.1 mg/m^3 using approximately 20-L sample volumes [3] of a generated atmosphere of epichlorohydrin. During sampling, a total hydrocarbon analyzer was used to independently verify the analyte concentration. Epichlorohydrin at the OSHA standard, 0.38 mg, was stable on coconut charcoal for six days at ambient temperature. Over the analytical range, the average DE was 0.905. Breakthrough of the front section occurred at 44.4 L while sampling 43.1 mg/m^3 at 0.185 L/min.

Epichlorohydrin was also sampled at 40 µg/L for 49 L without breakthrough to the back section using 80% relative humidity [2]. In this later evaluation, epichlorohydrin on lot 105, PCB 20/40, charcoal was found to be stable for at least two weeks. A DE of 0.82 was used to correct results of 8.1 and 11.6 µg per tube.

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Epichlorohydrin, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-206 (1976).
[2] Hill, R. H., Jr., J. A. Arnold and W. J. Woodfin. Collection and Deterination of Epichlorohydrin in Air, NIOSH, Method evaluation report (unpublished, 1976).
[3] Documentation of the NIOSH Validation Tests, S118, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).

[4] NIOSH Manual of Analytical Methods, 2nd. ed., V. 2, S118, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[5] Ibid, V. 1, P&CAM 127, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).

METHOD REVISED BY: James E. Arnold, NIOSH/DPSE; S118 validated under NIOSH Contract CDC-99-74-45.

(1) EPN, (2) MALATHION, and (3) PARATHION

FORMULA: (1) $C_{14}H_{14}NO_4PS$
(2) $C_{10}H_{19}O_6PS_2$
(3) $C_{10}H_{14}NO_5PS$
M.W.: (1) 323.31; (2) 330.36; (3) 291.27

METHOD: 5012
ISSUED: 2/15/84

OSHA/NIOSH/ACGIH: Table 1

PROPERTIES: Table 2

SYNONYMS: (1) EPN: phenylphosphonothioic acid O-ethyl O-p-nitrophenyl ester; CAS#2104-64-5; (2) Malathion: [(dimethoxyphosphinothioyl)thio]butanedioic acid diethyl ester; CAS# 121-75-5; (3) Parathion: phosphorothioic acid O,O-diethyl O-(4-nitrophenyl)ester; CAS# 56-38-2.

SAMPLING

SAMPLER: FILTER
(glass fiber)

FLOW RATE: 1 to 2 L/min

VOL-MIN: 15 L
-MAX: (1) 700 L; (2) 130 L; (3) 700 L

FIELD TREATMENT: transfer filters within 1 hr of sampling to vial; add 15 mL isooctane if Malathion present

SHIPMENT: in vials

SAMPLE STABILITY: at least 7 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: (1) 0.3 to 1.2 mg/m³ [1];
(2) 8 to 35 mg/m³ [2];
(3) 0.07 to 0.3 mg/m³ [1]
(120-L samples)

BIAS: not significant [1]

OVERALL PRECISION (s_r): 0.06 to 0.08 [1,2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FLAME PHOTOMETRIC

ANALYTE: EPN, Malathion, Parathion

DESORPTION: 15 mL isooctane

INJECTION VOLUME: 5 µL

	(1)	(2)	(3)
TEMPERATURE-INJECTION:	215 °C	240 °C	215 °C
-DETECTOR:	215 °C	200 °C	200 °C
-COLUMN:	205 °C	185 °C	165 °C

CARRIER GAS: N_2 or He, 60 mL/min

COLUMN: 2 m x 6 mm glass, packed with 3% OV-1 on on 100/120 mesh Gas Chrom Q for (1) and (3); 1.5% OV-17 + 1.95% OV-210 on 80/100 mesh Gas Chrom Q for (2)

CALIBRATION: solutions of the analytes in isooctane

RANGE: (1) 0.006 to 0.17 mg per sample;
(2) 0.14 to 4 mg per sample;
(3) 0.001 to 0.04 mg per sample

ESTIMATED LOD: (1), 2 ng; (2) or (3), 4 ng per sample [1,2]

PRECISION (s_r): 0.02 to 0.04 [1,2]

APPLICABILITY: The working range is 0.05 to 1.5 mg/m³ EPN, 1 to 30 mg/m³ Malathion, and 0.01 to 0.3 mg/m³ Parathion for 120-L air samples.

INTERFERENCES: None known.

OTHER METHODS: This method combines and replaces Methods S285, S295 and S370 [3]. The method of Hill and Arnold [4] has also been used for analysis of pesticides.

REAGENTS:

1. EPN, Malathion, and Parathion.*
2. Isooctane, chromatoquality.*
3. Calibration stock solutions (prepare fresh daily):
   a. EPN, 15 mg/mL, in isooctane.
   b. Malathion, 450 mg/mL, in dimethylformamide.
   c. Parathion, 3.3 mg/mL, in isooctane.

   NOTE: 4 µL of each solution contains a mass of analyte equivalent to a 120-L air sample at OSHA PEL (0.06 mg EPN, 1.8 mg Malathion, and 0.0132 mg Parathion).
4. Nitrogen, purified.
5. Hydrogen, prepurified.
6. Oxygen, purified.
7. Air, filtered, compressed.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass fiber filter (Gelman Type AE or equivalent), 37-mm, in a two-piece polystyrene cassette supported by a backup pad.
2. Personal sampling pump, 1 to 2 L/min, with flexible connecting tubing.
3. Gas chromatograph, column bypass valve, flame photometric detector phosphorus filter, integrator and column (page 5012-1).
4. Vials, 20-mL, glass with PTFE-lined caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Volumetric flasks, 10-mL.
7. Pipets, 15-mL, with pipet bulb.
8. Tweezers.

SPECIAL PRECAUTIONS: EPN, Malathion, and Parathion are highly toxic cholinesterase inhibitors with cumulative effects [5,6,7]. Special care must be taken to avoid inhalation or skin contact.

Isooctane is flammable. Prepare all samples in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at 1 to 2 L/min for 1 to 2 hrs (120-L sample is recommended). Do not exceed 2 mg total dust loading on the filter.
3. Within 1 hr after sampling, transfer the glass fiber filter with tweezers to a clean 20-mL vial. If sampling for Malathion, add 15 mL isooctane to the vial immediately after sampling. Mark the level of isooctane.

SAMPLE PREPARATION:

4. Pipet 15 mL isooctane into each vial. Cap each vial and swirl the contents for 1 hr.
   NOTE: Do not add isooctane to the Malathion sample vials which have had isooctane added in the field.

CALIBRATION AND QUALITY CONTROL:

5. Prepare at least five working standards covering the analytical range of the method, by diluting aliquots of the calibration stock solutions to 15 mL with isooctane.
   a. Analyze calibration standards in triplicate with the unknowns, blanks and other quality control spiked samples following steps 7 through 9.
   b. Prepare calibration graph by plotting peak area or peak height vs. mg of analyte.

6. Analyze control samples with each sample set, in duplicate.
   a. To prepare control samples, place a filter media blank in a clean 20-mL vial.
   b. Inject analyte calibration stock solution directly onto the filter with a microliter syringe.
      NOTE: If analyzing for Malathion, extract the filters with 15 mL isooctane before allowing to stand overnight.
   c. Cap the vial and allow to stand overnight.
   d. Analyze according to steps 4 and 7 through 9.
   e. Calculate recovery (mg found on filter divided by mg added to filter).

MEASUREMENT:

7. Set gas chromatograph to conditions given on page 5012-1, optimizing the air, hydrogen and oxygen according to the GC manufacturer's instructions.
8. Inject 5-µL sample aliquots using solvent flush technique.
   a. Vent the solvent peak by opening the column bypass valve at the time of injection. Close the column bypass valve after the solvent peak has eluted (ca. 30 sec) and before the analyte peak elutes.
   b. Make replicate injections of samples and standards.
9. Measure peak area or peak height.

CALCULATIONS:

10. Read the mass, mg per sample, of analyte found on the sample filters, W, and average media blank filters, B, from the calibration graph.
11. Calculate the concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W - B) \cdot 10^3}{V}, \text{ mg/m}^3$$

EVALUATION OF METHOD:

Method S285 for EPN was issued on April 26, 1976 [3]. Method S370 for Malathion was issued on September 30, 1976 [3]. Method S295 for Parathion was issued on March 26, 1976 [3].

The precision and accuracy listed below were obtained by generating atmospheres of the analytes at one-half, one and two times their OSHA standards [1,2,8]. Test atmospheres were generated using Trion-6 EPN (Wilbur Ellis Co.), Malathion-50 (Ortho) and Aqua-8 Parathion (FMC Corp.). Gelman Type AE glass fiber filters were used for all sampling and measurement recovery studies. Collection efficiency of the glass fiber filter was determined to be 1.0 for all three analytes and losses from vaporization of known amounts of the analytes deposited on a glass fiber filter were negligible [7,9] confirmed later for Parathion by Hill and Arnold using a different sampling device [4]. Filters spiked with solutions of EPN or Parathion gave quantitative recoveries after storage for 7 days at 25 °C. Samples containing Malathion gave 88% recovery if stored on filters for 7 days and 100% if the samples were desorbed with isooctane soon after sampling before storage.

		Precision, s_r		Range Studied		
Compound	Method	Overall	Measurement	mg/m³ (120-L sample)	mg per sample	Recovery
EPN	S285	0.059	0.037	0.3 to 1.2	0.03 to 0.12	1.00
Malathion	S370	0.063	0.036	8 to 35	0.9 to 3.6	1.03
Parathion	S295	0.078	0.015	0.07 to 0.26	0.0066 to 0.026	1.00

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S285 and S295, U.S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).

[2] Backup Data Report S370, prepared under NIOSH Contract 210-76-0123, available as Order No. PB 271-712 from NTIS, Springfield, VA 22161 (1976).

[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3, S285, S370 and S295, U.S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

[4] Hill, Robert H., Jr. and James E. Arnold. A Personal Air Sampler for Pesticides, Arch. Environm. Contam. Toxicol., 8, 621-628 (1979).

[5] Criteria for a Recommended Standard...Occupational Exposure to Malathion, U.S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 76-205 (1976).

[6] Criteria for a Recommended Standard...Occupational Exposure to Parathion, U.S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 76-190 (1976).

[7] Criteria for a Recommended Standard...Occupational Exposure During the Manufacture and Formulation of Pesticides, U.S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 78-174 (1978).

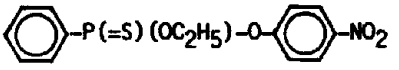
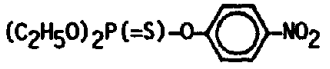
[8] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

[9] Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1983-84, American Conference of Governmental Industrial Hygienists, Cincinnati, OH (1983).

[10] Pocket Guide to Chemical Hazards, pp. 94, 122, 148, U.S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 78-210 (1978).

METHOD REVISED BY: Paula Fey O'Connor, NIOSH/DPSE; Methods S285 and S295 originally validated under NIOSH Contract CDC 99-74-45; S370 originally validated under NIOSH Contract 210-76-0123.

Table 1. Formula and exposure limits.

Compound	Structure	Exposure Limit (mg/m³; all have "skin" notation) OSHA	NIOSH*	ACGIH [9]
EPN		0.5	Group I Pesticide	0.5, STEL 2
Malathion	$(CH_3O)_2P(=S)SCH(COOC_2H_5)-CH_2COOC_2H_5$	15	15 [5]; Group II Pesticide	10
Parathion		0.1	0.05 [6]; Group I Pesticide	0.1, STEL 0.3

*Blood monitoring required [7].

Table 2. Properties.

Compound	Liquid Density @ 25 °C (g/mL)	BP (°C)	MP (°C)	VP, Pa (mm Hg; mg/m³) [10]
EPN	1.268	not available	36	0.04 (0.0003; 5) @ 100 °C
Malathion	1.23	156	2.9	0.005 (0.00004; 0.7) @ 20 °C
Parathion	1.26	375	6	0.05 (0.0004; 6) @ 20 °C

FORMULA: Table 2

M.W.: Table 1

ESTERS I

METHOD: 1450
ISSUED: 2/15/84

OSHA/NIOSH/ACGIH: Table 2

PROPERTIES: Table 2

COMPOUNDS: (synonyms in Table 2)
- n-amyl acetate
- sec-amyl acetate
- n-butyl acetate
- sec-butyl acetate
- t-butyl acetate
- 2-ethoxyethyl acetate
- ethyl acrylate
- isoamyl acetate
- isobutyl acetate
- methyl isoamyl acetate
- n-propyl acetate

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L @ OSHA standard
-MAX: 10 L

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.5 to 2X OSHA [2]
(10-L samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.05 to 0.09 [2];
see EVALUATION OF METHOD

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 1 mL CS_2, 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 200 - 225 °C
-DETECTOR: 250 - 300 °C
-COLUMN: 60 to 100 °C (Table 1)

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: stainless steel, 3 m x 3 mm, 5% FFAP on 100/120 mesh Chromosorb WHP

CALIBRATION: solutions of compounds in CS_2

RANGE: Table 1

ESTIMATED LOD: 0.02 mg per sample [3]

PRECISION (s_r): 0.02 [2]

APPLICABILITY: This method can be used for simultaneous analysis of 2 or more substances by changing the gas chromatographic conditions (e.g., temperature programming). High humidity greatly reduces sampler capacity and breakthrough volume.

INTERFERENCES: None identified. Alternate columns (e.g., 10% SP-1000 on Chromosorb WHP may be useful if interferences are encountered.

OTHER METHODS: This method combines and replaces Methods S31, S32, S35, S37, S41, S44 through S48, and S51 [1,2].

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REAGENTS:

1. Eluent: Carbon disulfide* (chromatographic grade) with 0.1% (v/v) benzene or 1% (v/v) tridecane, dodecane, undecane or other suitable internal standard.
2. Analyte, reagent grade.
3. Helium, purified.
4. Hydrogen, prepurified.
5. Air, compressed, filtered.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1450-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10-µL, readable to 0.1 µL, 25-, 50- and 100-µL.
6. Volumetric flasks, 10-mL.
7. Pipet, volumetric, 1-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 1 to 10 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.02 to 10 mg analyte per sample.
   a. Add known amounts of analyte to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of analyte directly onto front sorbent section with a microliter syringe.

c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg analyte recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1450-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

The methods listed below were issued on December 6, 1974, except for S51, which was issued on January 17, 1975 [1]. Atmospheres of each compound were generated in dry air by calibrated syringe drive and 10-L air samples were taken [2]. Spiked samplers were used to study measurement precision and desorption efficiency (DE). Results are as follows:

		Overall			Measurement		
Compound	Method [1,2]	Range, mg/m³	Breakthrough[1]	s_r	Range, mg per sample	DE[2]	s_r
n-amyl acetate	S51	208-871	34.2	0.051	2.6-10	0.87	0.019
sec-amyl acetate	S31	349-1460	20.9	0.071	3.3-13	0.93	0.012
n-butyl acetate	S47	352-1475	20.5	0.069	3.5-14	0.94	0.020
sec-butyl acetate	S46	478-2005	16.5	0.054	4.7-19	0.93	0.017
t-butyl acetate	S32	424-1780	14.3	0.091	4.7-19	0.94	0.039
2-ethoxyethyl acetate	S41	262-1100	34.6	0.062	2.5-11	0.79	0.024
ethyl acrylate	S35	50-210	>45	0.054	0.5-2	0.95	0.029
isoamyl acetate	S45	208-874	32.3	0.056	2.6-10	0.91	0.010
isobutyl acetate	S44	306-1280	21.5	0.065	3.5-14	0.94	0.016
methyl isoamyl acetate	S37	143-601	>45	0.058	1.5-6	0.93	0.021
n-propyl acetate	S48	384-1610	17.9	0.056	4.2-17	0.93	0.018

[1]5% breakthrough, 0.2 L/min, at high end of concentration range in dry air.
[2]Averaged over mass range shown.

REFERENCES:
[1] NIOSH Manual of Analytical Methods, 2nd ed., V. 2, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[2] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[3] User check, UBTL, NIOSH Sequence #4121-N (unpublished, November 15, 1983).

METHOD REVISED BY: Robert W. Kurimo, NIOSH/DPSE; methods originally validated under NIOSH Contract CDC-99-74-45.

Table 1. Operational details.

Compound	M.W.; mg/m^3 = 1 ppm @ NTP	Working range mg/m^3 @ 10 L	Measurement Range, mg per sample	Column Temperature, °C
n-amyl acetate	130.18; 5.32	50 to 1575	0.5 to 16	90
sec-amyl acetate	130.18; 5.32	65 to 1950	0.65 to 20	95
n-butyl acetate	116.16; 4.75	71 to 2130	0.7 to 21	90
sec-butyl acetate	116.16; 4.75	95 to 2850	1 to 28	60
t-butyl acetate	116.16; 4.75	95 to 2850	1 to 28	70
2-ethoxyethyl acetate	132.16; 5.40	54 to 1620	0.5 to 16	100
ethyl acrylate	100.11; 4.09	10 to 300	0.1 to 3	70
isoamyl acetate	130.18; 5.32	50 to 1575	0.5 to 16	90
isobutyl acetate	116.16; 4.75	70 to 2100	0.7 to 21	70
methyl isoamyl acetate	144.22; 5.90	30 to 900	0.3 to 9	90
n-propyl acetate	102.13; 4.18	84 to 2520	0.8 to 25	70

Table 2. General information.

Compound and Formula	Synonyms	OSHA/NIOSH/ACGIH (ppm)	BP (°C)	VP @ 20°C, kPa (mm Hg)	Liquid Density, g/mL @ 20 °C
n-amyl acetate $CH_3COO(CH_2)_4CH_3$; $C_7H_{14}O_2$	acetic acid 1-pentanol ester; CAS #628-63-7	100/ — /100	142	0.5(4)	0.879
sec-amyl acetate $CH_3COOCHCH_3(CH_2)_2CH_3$; $C_7H_{14}O_2$	acetic acid 2-pentanol ester; CAS #626-38-0	125/ — /125	134	0.9(7)	0.898
n-butyl acetate $CH_3COO(CH_2)_3CH_3$; $C_6H_{12}O_2$	acetic acid butyl ester; CAS #123-86-4	150/ — /150	125	1.3(10)	0.881
sec-butyl acetate $CH_3COOCH(CH_3)CH_2CH_3$; $C_6H_{12}O_2$	acetic acid 1-methyl propyl ester; CAS #105-46-4	200/ — /200	112	1.3(10)	0.865
t-butyl acetate $CH_3COOC(CH_3)_3$; $C_6H_{12}O_2$	acetic acid 1,1-dimethylethyl ester; CAS #540-88-5	200/ — /200	98	not available	0.867
2-ethoxyethyl acetate $CH_3COO(CH_2)_2OCH_2CH_3$; $C_6H_{12}O_3$	Cellosolve acetate; acetic acid ethylene glycol monoethyl ether ester; CAS #111-15-9	100*/ — /50*	156	0.3(2)	0.973
ethyl acrylate $CH_2=CHCOOCH_2CH_3$; $C_5H_8O_2$	2-propenoic acid ethyl ester; CAS #140-88-5	25/ — /5*	99	3.9(30)	0.941
isoamyl acetate $CH_3COO(CH_2)_2CH(CH_3)_2$; $C_7H_{14}O_2$	acetic acid 3-methyl-1-butanol ester; CAS #123-92-2	100/ — /100	142	0.5(4)	0.876 (15 °C)
isobutyl acetate $CH_3COOCH_2CH(CH_3)_2$; $C_6H_{12}O_2$	acetic acid isobutyl ester; CAS #110-19-0	150/ — /150	117	1.7(13)	0.871
methyl isoamyl acetate $CH_3COOCH(CH_3)CH_2CH(CH_3)_2$; $C_8H_{16}O_2$	acetic acid 4-methyl-2-pentanol ester; 1,3-dimethyl butyl acetate; "sec-hexyl acetate"; CAS #142-92-7	50/ — /50	141	0.5	0.858
n-propyl acetate $CH_3COO(CH_2)_2CH_3$; $C_5H_{10}O_2$	acetic acid n-propyl ester; CAS #109-60-4	200/ — /200	102	33(25)	0.836

*Skin

FORMULA: BrH_2CCH_2Br; $C_2H_4Br_2$

M.W.: 187.88

ETHYLENE DIBROMIDE

METHOD: 1008
ISSUED: 2/15/84

OSHA: 0.1 ppm; C 0.5 ppm (proposed)
NIOSH: 1 mg/m³/15 min [1]
ACGIH: carcinogen (skin)
(1 ppm = 7.68 mg/m³ @ NTP)

PROPERTIES: liquid; d 2.169 g/mL @ 25 °C;
BP 131 °C; MP 10 °C;
VP 1.5 kPa (11 mm Hg; 1.4% v/v) @ 25 °C

SYNONYMS: EDB, 1,2-dibromoethane; CAS #106-93-4.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.02 to 0.2 L/min

VOL-MIN: 0.1 L @ 0.1 ppm
-MAX: 25 L

SAMPLE STABILITY: refrigerated samples (-25 °C or below) may be stored 2 weeks [3,4]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD [3]

BIAS: not significant [4]

OVERALL PRECISION (s_r): not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ^{63}Ni ECD

ANALYTE: ethylene dibromide

DESORPTION: 10 mL 99:1 benzene:methanol (v/v); stand 1 hr

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 175 °C
-DETECTOR: 315 °C
-COLUMN: 50 °C

CARRIER GAS: N_2, 35 mL/min

COLUMN: 1.8 m x 4 mm ID, borosilicate glass packed with 3% OV-210 on 80/100 Gas Chrom Q

CALIBRATION: ethylene dibromide in 99:1 benzene:methanol (v/v) with internal standard

RANGE: 0.04 to 0.8 µg per sample [3]

ESTIMATED LOD: 0.01 µg per sample [3]

PRECISION (s_r): 0.044 [4]

APPLICABILITY: The working range is 0.0003 to 1 ppm (0.002 to 8 mg/m³) for a 25-L air sample. The range of an ECD most useful for quantitation depends on the type of detector and chromatograph used. For reliable quantitation, the ECD must be optimized for the smallest possible amount of analyte.

INTERFERENCES: None identified. The chromatographic column or separation conditions may be changed to circumvent interference problems. An alternate chromatographic column packing is GP 20% SP-2100/0.1% Carbowax 1500 on 100/120 Chromosorb WHP.

OTHER METHODS: This is P&CAM 260 [3] in a revised format. Method S104 [2], which has not been revised, can also be used but uses the less sensitive flame ionization detector.

REAGENTS:

1. Benzene, pesticide quality.*
2. Methanol, pesticide quality.*
3. Ethylene dibromide, high purity (density=2.169 g/mL @ 25 °C).*
4. An appropriate internal standard such as 1,1,2,2-tetrachloroethane (density=1.587 g/mL @ 25 °C) or 1,2-dibromopropane (density= 1.923 g/mL @ 25 °C).
5. 99:1 benzene:methanol (v/v).
6. Eluent*: 99:1 benzene:methanol (v/v) containing 0.08 mg internal standard/mL.
7. Calibration stock solution, 10 ng/µL. Dissolve 50 mg ethylene dibromide in benzene to make 25 mL solution. Dilute 50 µL of this solution to 10 mL with benzene

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing two sections of 20/40 mesh activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.02 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, ^{63}Ni electron-capture detector, integrator and column (see page 1008-1).
4. Syringes, 10-µL, readable to 0.1 µL and 50-µL, readable to 1 µL.
5. Volumetric flasks, 10-mL, 25-mL, and 500-mL.
6. Pipet, 10-mL with pipet bulb.

SPECIAL PRECAUTIONS: Benzene and ethylene dibromide [1] are carcinogens and can be absorbed through the skin. Benzene and methanol are flammable. All work with these should be performed in a hood, while wearing gloves.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.02 and 0.2 L/min for a total sample size of 0.1 to 25 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely in an insulated container with dry ice for shipment.

SAMPLE PREPARATION:

NOTE: Store the samplers at -25 °C or below until preparation begins.

5. Place the front and back sorbent sections of the sampler tube in separate 10-mL volumetric flasks. Discard the glass wool and foam plugs.
6. Add 10.0 mL eluent to each flask.
7. Allow to stand 60 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.01 to 0.8 µg ethylene dibromide per sample.
   a. Add known amounts of calibration stock solution to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).

c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. µg ethylene dibromide).

9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. µg ethylene dibromide recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1008-1. Inject sample aliquot manually using solvent flush technique or with autosampler. Retention times under these conditions are: ethylene dibromide, 2.2 min; 1,2-dibromo propane, 2.9 min; and 1,1,2,2-tetrachloroethane, 4.1 min.
    NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE) of ethylene dibromide found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of ethylene dibromide in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method P&CAM 260 [3] was evaluated with coconut shell charcoal (SKC Lot 106 and MSA Lot 6) fortified with solutions of ethylene dibromide. Average recoveries ranged from 0.85 to 0.93; overall precision (s_r) was 0.044 (31 samples, pooled) [4]. Samples based on 0.2- and 2-µg quantities of ethylene dibromide were stable on charcoal during storage below -20 °C for 13 and 12 days, respectively. Gasoline samples which contained ethylene dibromide were placed into U-tubes; ethylene dibromide vapor was collected with charcoal tubes (flow rate of air was 0.6 L/min). Recoveries were 0.91 and 0.93 for 0.2- and 2.4-µg quantities of ethylene dibromide, respectively. No significant breakthrough from front sections of charcoal occurred with 200-µg quantities of ethylene dibromide in the vapor phase (flow rate of air was 0.6 L/min); quantities of ethylene dibromide (if any) on the back sections of charcoal were less than 0.04 µg (<0.02%).

Breakthrough was determined for SKC Lot 105 charcoal [5]. At a concentration of 446 mg ethylene dibromide/m³ in dry air, the effluent concentration was 2% of the test concentration after 4 hrs of sampling (48 L air). Thus, the capacity of the charcoal was at least 21 mg ethylene dibromide under these conditions.

REFERENCES:
[1] Criteria for a Recommended Standard...Occupational Exposure to Ethylene Dibromide, U.S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 77-221 (1977).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 2, S104, U.S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[3] Ibid, V. 4, P&CAM 260, U.S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[4] Tucker, S. P., J. J. Sweeney and A. W. Teass. "A Charcoal Tube Method for Determining 1,2-Dibromoethane in Air," NIOSH (unpublished, 1979).
[5] Documentation of the NIOSH Validation Tests, S104, U.S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).

METHOD REVISED BY: K. J. Williams, NIOSH/DPSE.

FORMULA: $HOCH_2CH_2OH$; $C_2H_6O_2$

M.W.: 62.07

ETHYLENE GLYCOL

METHOD: 5500
ISSUED: 2/15/84

OSHA: no standard
NIOSH: no standard
ACGIH: C 50 ppm
(1 ppm = 2.54 mg/m³ @ NTP)

PROPERTIES: liquid; BP 198 °C; d 1.1135 g/mL @ 20 °C;
VP 13 Pa (0.1 mm Hg; 130 ppm) @ 25 °C

SYNONYMS: 1,2-ethanediol; CAS #107-21-1.

SAMPLING

SAMPLER: FILTER + SORBENT
(glass fiber filter + silica gel, 520 mg/260 mg)

FLOW RATE: 0.2 L/min

VOL-MIN: 0.3 L
-MAX: 60 L

SHIPMENT: filter in glass vial with 1 mL 2:98 2-propanol:H_2O directly after sampling; silica gel tube sealed with plastic caps

SAMPLE STABILITY: ≥ 15 days @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 45 to 98 mg/m³ [1]

BIAS: not significant [1]

OVERALL PRECISION (s_r): 0.084 (aerosol);
0.087 (vapor) [1]

MEASUREMENT

!
!TECHNIQUE: GAS CHROMATOGRAPHY, FID
!
!ANALYTE: ethylene glycol
!
!SILICA GEL DESORPTION: 1 mL 2:98
! 2-propanol:H_2O;
! stand 5 min
!
!INJECTION VOLUME: 1 µL
!
!TEMPERATURE-INJECTION: 250 °C
! -DETECTOR: 300 °C
! -COLUMN: 165 °C
!
!CARRIER GAS: N_2 or He, 30 mL/min
!
!COLUMN: glass, 1.9 m x 2 mm; 3% Carbowax 20M
! on 80/100 Chromosorb 101
!
!CALIBRATION: solutions of ethylene glycol in
! 2:98 2-propanol:H_2O (v/v)
!
!RANGE: 0.02 to 1 mg per sample
!
!ESTIMATED LOD: 4 µg per sample
!
!PRECISION (s_r): 0.060 (filters);
! 0.080 (silica gel) [1]
!

APPLICABILITY: The working range is 7 to 330 mg/m³ for a 3-L air sample.

INTERFERENCES: A ghosting phenomenon which was described by Spitz [2] caused little or no error in measurements when samples were analyzed with standards at similar concentrations.

OTHER METHODS: This method originally was designated P&CAM 338 [3] and was evaluated with a reference method which involved sampling with bubblers of water, oxidation of ethylene glycol to formaldehyde with periodic acid and colorimetric analysis [1].

REAGENTS:

1. Ethylene glycol.
2. 2-Propanol:water, 2:98 (v/v). Add 2 volumes 2-propanol to 98 volumes freshly distilled water.
3. Helium or nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, filtered.
6. Calibration stock solution, 10 mg/mL, in 2:98 2-propanol:water.

EQUIPMENT:

1. Sampler: 13-mm glass fiber filter, free of binders, in filter holder (Cat. No. SX00 013 00, Millipore Corp. or equivalent) followed by glass tube, 8 cm long, 8 mm OD, 6 mm ID; two sections of 20/40 mesh silica gel (d = 0.72 g/cm^3; surface area, 720 to 760 m^2/g) separated by 3-mm urethane foam plug (front = 520 mg; backup = 260 mg). Filter holder and glass tube connected with two short pieces of plastic tubing. One piece (7 mm long) fits tightly around outlet of filter holder; other piece fits over first piece and inlet of glass tube.
2. Personal sampling pump, 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 5500-1).
4. Vials, glass, 1-mL, rubber caps.
5. Syringes, 10-µL, readable to 0.1 µL.
6. U-tube, glass, 25 cm x 15 mm ID.
7. Constant temperature bath, 75 °C.
8. Volumetric flasks, 10-mL

SPECIAL PRECAUTIONS: None.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at 0.2 L/min for a total sample size of 0.3 to 60 L.
3. Immediately after sampling, disassemble the sampler and transfer the filter to a vial containing 1 mL 2:98 2-propanol:water. Seal the vial.
4. Seal the ends of the silica gel tubes with plastic caps.

SAMPLE PREPARATION:

5. Transfer front and backup sections of silica gel to separate vials. Add 1 mL 2:98 2-propanol:water to each vial.
6. Agitate vials occasionally for 5 min.

CALIBRATION AND QUALITY CONTROL:

7. Calibrate daily with at least five working standards over the range 0.003 to 1 mg ethylene glycol per sample.
   a. Add known amounts of calibration stock solution to 2:98 2-propanol:water in 10-ml volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 10 through 12).
   c. Prepare calibration graph (peak area or height vs. mg ethylene glycol).
8. Determine recovery from filters in the calibration range (step 7). Prepare three filters at each of three levels plus three media blanks.
   a. Place a filter in a clean vial.
   b. Add a known quantity of ethylene glycol in 5 µL water solution to the filter.
   c. Seal the vial; let stand 30 min.
   d. Prepare and analyze the filters together with working standards (steps 5 and 6 and 10 through 12).

e. Calculate recovery (ethylene glycol recovered/ethylene glycol taken).

9. Determine DE from silica gel for each lot of silica gel in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
   a. Draw ethylene glycol vapor with a pump at 0.2 L/min into sampler tubes from a U-tube partly immersed in a constant temperature bath at 75 °C.
      NOTE: Values of DE for liquid and vapor spikes may be different [1].
   b. Desorb (steps 5 and 6) and analyze (steps 10 through 12) together with working standards.
   c. Prepare a graph of DE vs. mg ethylene glycol recovered.

MEASUREMENT:

10. Set gas chromatograph according to conditions given on page 5500-1. Set flow rates of hydrogen and air according to manufacturer's instructions.
11. Inject sample aliquot manually using solvent flush technique or with autosampler. t_r = 4 min for these conditions.
12. Measure peak area or peak height.

CALCULATIONS:

13. Determine the mass, mg (corrected for recovery or DE) of ethylene glycol found on the filter (W) and in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank filter (B), and front (B_f) and back (B_b) sorbent sections.
14. Calculate concentration, C, of ethylene glycol in the air volume sampled, V (L):

$$C = \frac{(W + W_f + W_b - B - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

The method was tested with spiked samplers and atmospheres generated with a diffusion cell and verified with bubblers of water and colorimetric analysis for 54 to 98 mg/m³. s_r = 0.084 (six samples) for 6-L samples at 14 mg/m³ (aerosol); s_r = 0.087 (17 samples, pooled) for 6-L samples at 45 to 84 mg/m³ (vapor). Breakthrough (79 mg/m³, 0.2 L/min) = 261 L; recovery from filters (20 to 900 µg per sample) = 1.03; DE from silica gel (20 to 3120 µg per sample) = 0.81 to 0.87; storage stability = 49% of 85 µg evaporated from filters during 4 hrs at 24 °C, 78 µg stable on silica gel for 15 days at 25 °C. Area samples were collected side-by-side for 4 hrs at a field location by this method and a reference method (bubblers and colorimetric analysis); concentrations by this method, 0.63, 0.59, and 0.23 mg/m³, were 1.4, 0.7 and 26.5% higher than corresponding concentrations by the reference method [1].

REFERENCES:

[1] Tucker, S. P., and G. J. Deye. Anal. Lett., 14 (A12), 959-976 (1981).
[2] Spitz, H. D. J. Pharm. Sci., 61, 1339-1340 (1972).
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 7, P&CAM 338, U.S. Department of Health and Human Services, Publ. (NIOSH) 82-100 (1981).

METHOD WRITTEN BY: Samuel P. Tucker, Ph.D., and Gregory J. Deye, NIOSH/DPSE.

FORMULA: ; $C_3H_6N_2S$

M.W.: 102.17

ETHYLENE THIOUREA

METHOD: 5011
ISSUED: 2/15/84

OSHA: no standard
NIOSH: carcinogen/teratogen [1,2]
ACGIH: no standard

PROPERTIES: solid, MP 203 to 204 °C

SYNONYMS: 2-imidazolidinethione, ETU; CAS# 96-45-7.

SAMPLING

SAMPLER: FILTER
(5-µm PVC or mixed cellulose ester membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 200 L @ 0.05 mg/m³
-MAX: 800 L

SHIPMENT: routine

SAMPLE STABILITY: unknown

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: required; high-volume air or settled dust

ACCURACY

RANGE STUDIED: 0.03 to 1.5 mg/m³
(100-L sample)

BIAS: not significant [3]

OVERALL PRECISION (s_r): not determined

MEASUREMENT

TECHNIQUE: VISIBLE ABSORPTION SPECTROPHOTOMETRY

ANALYTE: ETU-pentacyanoammineferrate coordination complex

EXTRACTION: distilled water, stand 45 min @ 60 °C

COMPLEXATION: pentacyanoammineferrate reagent

WAVELENGTH: at 590 nm

CALIBRATION: solutions of ETU in water

RANGE: 10 to 150 µg per sample

ESTIMATED LOD: 0.75 µg per sample

PRECISION (s_r): 0.03%

APPLICABILITY: The working range is 0.05 to 0.75 mg/m³ for a 200-L air sample. Ethylene thiourea is used in the manufacture of fungicides, rubber vulcanization and in dyes, pharmaceuticals, synthetic resins and electroplating baths [3]. The method was also applied to tetramethyl thiourea [3].

INTEFERENCES: Compounds containing a thione (C=S) group will complex with the pentacyanoammineferrate reagent and may interfere with the ETU absorbance band at 590 nm.

OTHER METHODS: This method was originally designated P&CAM 281 [4], which it replaces.

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REAGENTS:

1. Bromine liquid, Br_2.*
2. Disodium pentacyanonitrosyl ferrate dihydrate (sodium nitroferricyanide; sodium nitroprusside), $Na_2Fe(CN)_5NO \cdot 2H_2O$.
3. Hydroxylamine hydrochloride, $NH_2OH \cdot HCl$.
4. Sodium bicarbonate, $NaHCO_3$.
5. Hexane.
6. Methanol.
7. Water, distilled or deionized.
8. Complexing reagent (see APPENDIX).
9. Dilute complexing reagent. Mix 1 volume complexing reagent with 2 volumes water. Prepare fresh daily.
10. Ethylene thiourea (ETU) (see APPENDIX).
11. Calibration stock solution, 1000 µg/mL. Dilute 0.250 g recrystallized ETU to 250 mL with distilled water.

*See Special Precautions.

EQUIPMENT:

1. Sampler: PVC filters, 5-µm pore size, 37-mm diameter or mixed cellulose ester filters, 0.8-µm pore size, 37-mm diameter; plastic filter holders (cassettes).
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Spectrophotometer to operate at 590 nm.
4. Matched glass cuvettes, 5-cm optical path length.
5. Analytical balance capable of weighing to the nearest 0.1 mg.
6. Mortar and pestle.
7. Waterbath thermostatically controlled to ± 1 °C.
8. Glass vials, 20-mL capacity, with PTFE-coated screw caps.
9. Beakers, assortment of 50- to 250-mL.
10. Adjustable pipettes (5- to 50-µL, 50- to 250-µL, 0.5- to 5-mL) with disposable tips.
11. Volumetric pipettes, assortment of 1- to 25-mL, with pipet bulb.
12. Volumetric flasks, 25-, 100-, 200- and 250-mL capacity.
13. Miscellaneous: tweezers, microspatula, rubber suction bulb, wood applicator stick weighing paper, filter paper and filter funnel with stand.

SPECIAL PRECAUTIONS: Bromine liquid is very corrosive and causes severe burns; vapors are extremely irritating and toxic. Wear gloves and handle only in a hood.

Ethylene thiourea is an animal teratogen and carcinogen [1,2]. Extra care must be taken to avoid inhalation, ingestion or skin contact. Keep ETU in a bottle labelled "animal carcinogen" and place the bottle in a resealable thick-walled plastic bag in locked storage.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 200 to 800 L. Do not exceed 2 mg dust loading on the filter.
3. Collect a high-volume air sample or rafter dust sample. Ship in a glass vial in a separate container from the filters.

SAMPLE PREPARATION:

4. Remove the top portion of the filter holder. Hold the bottom portion containing the filter and filter support over a piece of weighing paper. Remove the plug from the bottom of the filter holder and insert the applicator stick through the hole. Gently raise the filter and grasp the edge with tweezers. Very carefully transfer the filter to a 20-mL glass vial and push it gently to the bottom. Add to the vial any material remaining in the filter holder or collected on the weighing paper.

5. Pipet 7.0 mL distilled water into the vial to completely immerse the filter. Cap the vial.
6. Place vials in a 60 °C waterbath (thermostatically controlled) for 45 min. The waterbath level must be above the water level of the vial. Shake each vial every 5 min.
   NOTE: Do not use an ultrasonic bath because it breaks up the filters.
7. Lift the filter with tweezers above the water level in the vial. Wash the filter two times with 4-mL aliquots of water using a 5-mL adjustable pipette. Collect the rinsings in the vial. Discard the filter.

CALIBRATION AND QUALITY CONTROLS:

8. Standards.
   a. Prepare a 15 µg/mL ETU standard solution by pipetting 3.0 mL of the 1000 µg/mL calibration stock solution into a 200-mL volumetric flask and diluting to the mark with distilled water.
   b. Prepare working standards by pipetting 0- to 10-mL aliquots of the 15 µg/mL standard solution into clean vials. Bring the total volume to 15 mL with distilled water. Follow steps 10 and 11 to analyze the working standards.
   c. Prepare a calibration graph (absorbance vs. mass per sample).
9. Recovery Samples.
   a. On a plastic test tube rack, place eight filters. Using an adjustable pipette, add to the center of each filter 0, 7.5, 15, 30, 45, 60, 90, 120, and 150 µL of 1000-µg/mL calibration stock solution. Let filters air dry overnight at room temperature. Follow steps 4 through 7 and 10 through 11 for analysis of the spiked samples.
   b. Convert the absorbance of each sample to µg from the calibration graph. Calculate recovery, R (µg recovered/µg taken).

MEASUREMENT:

10. Complexation.
    NOTE: Perform this step at the same time for both standards and samples to reduce errors due to color degradation.
    a. Pipet a 1.5-mL aliquot of dilute complexing reagent into each vial.
    b. Allow the vials to stand for at least 30 min before analysis to insure full color development. Shake the vials every 10 min.
       NOTE: The color of the complexed samples varies with increasing concentration from yellow to light green to turquoise. Very high concentrations have Prussian blue color; in this case, the sample must be diluted before analysis.
11. Measurement.
    a. Transfer the solution to a clean 5-cm cuvette. Wipe off with a lens paper any droplets on the cuvette windows.
    b. Place the cell in the sample compartment and measure absorbance at 590 nm vs. a reference sample containing 15 mL distilled water and 1.5 mL dilute complexing reagent in a 5-cm cuvette. Record the absorbance for each sample.
       NOTE: Scan the absorbance of the bulk sample (processed according to steps 4 through 7 and 10 and 11) in the range 350 to 700 nm to detect possible interferences.

CALCULATIONS:

12. Determine the mass of ETU, µg (corrected for recovery), for the sample (M) and average media blank (B).
13. Calculate the concentration of ETU, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{(M - B)}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:
The method was tested with 21 PVC (VM-1)/ETU spiked samples in the range 15 to 150 µg per sample with an average recovery of 98.0 ± 3.2% [3]. It was also tested with 20 mixed cellulose ester filters spiked with ETU in the range of 15 to 150 µg per sample, giving an average recovery of 99.2% ± 3.6% [3]. All calibration graphs indicated a minimum linear correlation coefficient of 0.9999 [3]. The method was also used on 50 field samples on VM-1 filters in two surveys [3]. The amounts of ETU found ranged from 5 to 56 µg per sample.

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METHOD WRITTEN BY: John Palassis, NIOSH/DPSE.

APPENDIX:

1. PREPARATION OF COMPLEXING REAGENT
   a. Weigh 0.500 g $Na_2Fe(CN)_5NO \cdot 2H_2O$ in a 50-mL beaker. Dissolve in 10 mL distilled water.
   b. Grind together 0.500 g $NH_2OH \cdot HCl$ and 1.00 g $NaHCO_3$ in a mortar.
   c. In a hood, add the ground capacity mixture to the solution from (a.). When bubbling ceases, add 0.10 mL bromine. When reaction stops, add ca. 10 mL distilled water. Filter. Rinse beaker with 4 mL distilled water and filter. Transfer filtrate to a 25-mL volumetric flask and dilute with distilled water to the mark. Refrigerate. Stable at least two weeks at 4 °C [3].

2. PURIFICATION OF ETU
   a. In a 250-mL Erlenmeyer flask, weigh 3 to 5 g ETU. Dissolve in 100 mL 1:1 methanol:water. Heat to boiling in a hood. Cool 5 min at room temperature. Add 5 mL hexane. Shake 30 sec. Cover with watchglass. Let sit 1 hr at room temperature. Filter, washing with 100 mL 1:1 methanol:water. Let the crystals air dry in a hood.

FORMULA: various

M.W.: various

FIBERS

METHOD: 7400
ISSUED: 2/15/84

OSHA: 0.5 asbestos fibers (> 5 µm long)/mL
NIOSH: 0.1 asbestos f/mL [1]; 3 glass fibers (>10 µm x <3.5 µm)/mL [2]
ACGIH: 0.2 crocidolite; 0.5 amosite; 2 chrysotile and other asbestos, f/mL

PROPERTIES: solid, fibrous

SYNONYMS: asbestos (actinolite [CAS #13768-00-8], grunerite (amosite) [CAS #12172-73-5], anthophyllite [CAS #17068-78-9], chrysotile [CAS #12001-29-5], crocidolite [CAS #12001-28-4], tremolite [CAS #14567-73-8]); fibrous glass.

SAMPLING

SAMPLER: FILTER
(0.8-1.2 µm cellulose ester membrane, 25-mm diameter)

FLOW RATE*: ≥ 0.5 L/min

VOL-MIN*: 400 L @ 0.1 fiber/mL
-MAX*: 1920 L @ 0.1 fiber/mL
*Adjust for 100 to 1300 fibers/mm² (step 4)

SHIPMENT: routine

SAMPLE STABILITY: indefinite

BLANKS: 10% of samples (minimum 2) [3]

ACCURACY

RANGE STUDIED: 80 to 100 fibers counted

BIAS: see EVALUATION OF METHOD

OVERALL PRECISION (s_r): 0.115 to 0.13 [3] (A Rules)

MEASUREMENT

TECHNIQUE: MICROSCOPY, PHASE CONTRAST

ANALYTE: fibers (manual count)

SAMPLE PREPARATION: acetone/triacetin method

COUNTING RULES: Set A (P&CAM 239 [3,4]) or Set B (modified CRS [5])

EQUIPMENT: 1. phase-contrast microscope
2. Walton-Beckett graticule (100 µm field diameter): A Rules use G-22; B Rules use Type G-24
3. phase-shift test slide (HSE/NPL)

CALIBRATION: phase-shift detection limit about 3 degrees [7]

RANGE: 100 to 1300 fibers/mm² filter area [6]

ESTIMATED LOD: 7 fibers/mm² filter area

PRECISION: 0.10 to 0.12 [3] (A Rules)

APPLICABILITY: The working range is 0.02 fiber/mL (1920-L air sample) to 1.25 fibers/mL (400-L air sample). The method gives an index of airborne asbestos fibers but may be used for other materials such as fibrous glass by inserting suitable parameters into the counting rules. The method does not differentiate between asbestos and other fibers. Asbestos fibers less than ca. 0.25 µm diameter will not be detected by this method [7].

INTERFERENCES: Any other airborne fiber may interfere since all particles meeting the counting criteria are counted. Chain-like particles may appear fibrous. High levels of non-fibrous dust particles may obscure fibers in the field of view and raise the detection limit.

OTHER METHODS: This method introduces changes for improved sensitivity and reproducibility and replaces P&CAM 239 [3,4].

REAGENTS:

1. Acetone.*
2. Triacetin (glycerol triacetate), reagent grade.

*See Special Precautions.

EQUIPMENT:

1. Sampler: field monitor, 25 mm, three-piece cassette with 50-mm extension cowl with cellulose ester filter, 0.8 to 1.2-µm pore size and backup pad.
   NOTE: Analyze representative filters for fiber background before use and discard the filter lot if more than 5 fibers/100 fields are found.
2. Personal sampling pump, $\geq$ 0.5 L/min (see step 4 for flow rate), with flexible connecting tubing.
3. Microscope, phase contrast, with green or blue filter, 8 to 10X eyepiece, and 40 to 45X phase objective (total magnification ca. 400X); numerical aperture = 0.65 to 0.75.
4. Slides, glass, single-frosted, pre-cleaned, 25 x 75 mm.
5. Cover slips, 25 x 25 mm, no. 1-1/2, unless otherwise specified by microscope manufacturer.
6. Knife, #10 surgical steel, curved blade.
7. Tweezers.
8. Flask, Guth-type, insulated neck, 250 to 500 mL (with single-holed rubber stopper and elbow-jointed glass tubing, 16 to 22 cm long).
9. Hotplate, spark-free, stirring type; heating mantle; or infrared lamp and magnetic stirrer.
10. Syringe, hypodermic, with 22-gauge needle.
11. Graticule, Walton-Beckett type with 100 µm diameter circular field at the specimen plane (area = 0.00785 mm^2) (Type G-22 for A Rules; Type G-24 for B Rules). Available from Graticules Ltd., Morley Road, Tonbridge TN9 1RN, Kent, England (Telephone 011-44-732-359061).
    NOTE: The graticule is custom-made for each microscope. Specify disc diameter needed to fit exactly the ocular of the microscope and the diameter (mm) of the circular counting area (see step 11).
12. HSE/NPL phase contrast test slide, Mark II. Available from PTR Optics Ltd., 145 Newton Street, Waltham, MA 02154 (Telephone (617) 891-6000).
13. Telescope, ocular phase-ring centering.
14. Stage micrometer (0.01 mm divisions).

SPECIAL PRECAUTIONS: Acetone is an extremely flammable liquid and precautions must be taken not to ignite it. Heating of acetone must be done in a ventilated laboratory fume hood using a flameless, spark-free heat source.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line [3].
2. Fasten the sampler to the worker's lapel as close as possible to the worker's mouth. Remove the top cover from the end of the cowl extension (open face) and orient face down. Wrap the joint between the extender and monitor body with shrink tape to prevent air leaks.

3. Submit at least two field blanks (or 10% of the total samples, whichever is greater) for each set of samples. Remove the caps from the field blank cassettes and store the caps and cassettes in a clean area (bag or box) during the sampling period. Replace the caps in the cassettes when sampling is completed.
4. Sample at 0.5 L/min or greater [8]. Do not exceed 1 mg total dust loading on the filter. Adjust sampling flow rate, Q (L/min), and time to produce a fiber density, E (fibers/mm^2), of 100 to 1300 fibers/mm^2 [3.85 • 10^4 to 5 • 10^5 fibers per 25-mm filter with effective collection area (A_c= 385 mm^2)] for optimum counting precision (see step 21). Calculate the minimum sampling time, t_{min} (min), at the action level (one-half the current standard), L (fibers/mL), of the fibrous aerosol being sampled:

$$t_{min} = \frac{(A_c)(E)}{(Q)(L)10^3}.$$

5. Remove the field monitor at the end of sampling, replace the plastic top cover and small end caps, and store the monitor.
6. Ship the samples in a rigid container with sufficient packing material to prevent jostling or damage.
   NOTE: Do not use polystyrene foam in the shipping container because of electrostatic forces which may cause fiber loss from the sampler filter.

SAMPLE PREPARATION:

NOTE: The object is to produce samples with a smooth (non-grainy) background in a medium with a refractive index equal to or less than 1.46. The method below collapses the filter for easier focusing and produces permanent mounts which are useful for quality control and interlaboratory comparison. Other mounting techniques meeting the above criteria may also be used (e.g., the non-permanent field mounting technique used in P&CAM 239 [1,3,4]).

7. Ensure that the glass slides and cover slips are free of dust and fibers.
8. Place 40 to 60 mL of acetone into a Guth-type flask. Stopper the flask with a single-hole rubber stopper through which a glass tube extends 5 to 8 cm into the flask. The portion of the glass tube which exits the top of the stopper (8 to 10 cm) is bent downward in an elbow which makes an angle of 20 to 30° with the horizontal.
9. Place the flask on a stirring hotplate or wrap in a heating mantle. Heat the acetone gradually to its boiling temperature (ca. 58 °C).
   CAUTION: The acetone vapor must be generated in a ventilated fume hood away from all open flames and spark sources. Alternate heating methods can be used, providing no open flame or sparks are present.
10. Mount either the whole sample filter or a wedge cut from the sample filter on a clean glass slide.
    a. Cut wedges of ca. 25% of the filter area with a curved blade steel surgical knife using a rocking motion to prevent tearing.
    b. Place the filter or wedge, dust side up, on the slide. Static electricity will usually keep the filter on the slide until it is cleared.
    c. Hold the glass slide supporting the filter approximately 1 to 2 cm from the glass tube port where the acetone vapor is escaping from the heated flask. The acetone vapor stream should cause a condensation spot on the glass slide ca. 2 to 3 cm in diameter. Move the glass slide gently in the vapor stream. The filter should clear in 2 to 5 sec. If the filter curls, distorts or is otherwise rendered unusable, the vapor stream is probably not strong enough. Periodically wipe the outlet port with tissue to prevent liquid acetone dripping onto the filter.

d. Using the hypodermic syringe with a 22-gauge needle, place 1 to 2 drops of triacetin on the filter. Gently lower a clean 25-mm square cover slip down onto the filter at a slight angle to reduce the possibility of forming bubbles. If too many bubbles form or the amount of triacetin is insufficient, the cover slip may become detached within a few hours.

e. Glue the edges of the cover slip to the glass slide using a lacquer or nail polish [9].

NOTE: If clearing is slow, the slide preparation may be heated on a hotplate (surface temperature 50 °C) for 15 min to hasten clearing. Counting may proceed immediately after clearing and mounting are completed.

CALIBRATION AND QUALITY CONTROL:

11. Calibration of the Walton-Beckett graticule. The diameter, d_c (mm), of the circular counting area and the disc diameter must be specified when ordering the graticule.
    a. Insert any available graticule into the eyepiece and focus so that the graticule lines are sharp and clear.
    b. Set the appropriate interpupillary distance and, if applicable, reset the binocular head adjustment so that the magnification remains constant.
    c. Install the 40 to 45X phase objective.
    d. Place a stage micrometer on the microscope object stage and focus the microscope on the graduated lines.
    e. Measure the magnified grid length, L_o (μm), using the stage micrometer.
    f. Remove the graticule from the microscope and measure its actual grid length, L_a (mm). This can best be accomplished by using a stage fitted with verniers.
    g. Calculate the circle diameter, d_c (mm), for the Walton-Beckett graticule:

$$d_c = \frac{L_a}{L_o} \times D.$$

    Example: If L_o = 108 μm, L_a = 2.93 mm and D = 100 μm, then d_c = 2.71 mm.
    h. Check the field diameter, D(acceptable range 100 μm ± 2 μm) with a stage micrometer upon receipt of the graticule from the manufacturer. Determine field area (mm^2).
12. Microscope adjustments. Follow the manufacturer's instructions and also the following:
    a. Adjust the light source for even illumination across the field of view at the condenser iris.
    NOTE: Köhler illumination is preferred, where available.
    b. Focus on the particulate material to be examined.
    c. Make sure that the field iris is in focus, centered on the sample and open only enough to fully illuminate the field of view.
    d. Use the telescope ocular supplied by the manufacturer to ensure that the phase rings (annular diaphragm and phase-shifting elements) are concentric.
13. Check the phase-shift detection limit of the microscope periodically.
    a. Remove the HSE/NPL phase-contrast test slide from its shipping container and center it under the phase objective.
    b. Bring the blocks of grooved lines into focus.
    NOTE: The slide consists of seven sets of grooves (ca. 20 grooves to each block) in descending order of visibility from sets 1 to 7. The requirements for asbestos counting are that the microscope optics must resolve the grooved lines in set 3 completely, although they may appear somewhat faint, and that the grooved lines in sets 6 and 7 must be invisible. Sets 4 and 5 must be at least partially visible but may vary slightly in visibility between microscopes. A microscope which fails to meet these requirements has either too low or too high a resolution to be used for asbestos counting.

c. If the image quality deteriorates, clean the microscope optics and if the problem persists, consult the microscope manufacturer.

14. Quality control of fiber counts.
    a. Prepare and count field blanks along with the field samples. Report the counts on each blank. Calculate the mean of the field blank counts and subtract this value from each sample count before reporting the results.
       NOTE 1: The identity of the blank filters should be unknown to the counter until all counts have been completed.
       NOTE 2: If a field blank yields fiber counts greater than 7 fibers/100 fields, report possible contamination of the samples.
    b. Perform blind recounts by the same counter on 10% of filters counted (slides relabeled by a person other than the counter).
15. Use the following test to determine whether a pair of counts on the same filter should be rejected because of possible bias. This statistic estimates the counting repeatability at the 95% confidence level. Discard the sample if the difference between the two counts exceeds $2.77\ (F)s_r$, where F = average of the two fiber counts and s_r = relative standard deviation, which should be derived by each laboratory based on historical in-house data.
    NOTE: If a pair of counts is rejected as a result of this test, recount the remaining samples in the set and test the new counts against the first counts. Discard all rejected paired counts.
16. Enroll each new counter in a training course which compares performance of counters on a variety of samples using this procedure.
    NOTE: To ensure good reproducibility, all laboratories engaged in asbestos counting should participate in an asbestos proficiency testing program such as the NIOSH Proficiency Analytical Testing (PAT) Program and routinely participate with other asbestos fiber counting laboratories in the exchange of field samples to compare performance of counters.

MEASUREMENT:

17. Place the slide on the mechanical stage of the calibrated microscope with the center of the filter under the objective lens. Focus the microscope on the plane of the filter.
18. Regularly check phase-ring alignment and Köhler illumination [7].
19. Select one of the following sets of counting rules:
    NOTE: The two sets of rules have been demonstrated to produce equivalent mean counts on a variety of asbestos sample types [5] and must be strictly followed in order to obtain valid results. No hybridizing of the two sets of rules is permitted. The calibration of the microscope with the HSE/NPL test slide determines the minimum detectable fiber diameter (ca. 0.25 μm).
    a. A Rules (same as P&CAM 239 rules [1,3,4]).
       NOTE: The A Rules are required for monitoring asbestos for compliance purposes under OSHA or NIOSH standards.
       1. Count only fibers longer than 5 μm. Measure the length of curved fibers along the curve.
       2. Count only fibers with a length-to-width ratio equal to or greater than 3:1.
       3. For fibers which cross the boundary of the graticule field, do the following:
          a. Count any fiber longer than 5 μm which lies entirely within the graticule area.
          b. Count as 1/2 fiber any fiber with only one end lying within the graticule area.
          c. Do not count any fiber which crosses the graticule boundary more than once.
          d. Reject and do not count all other fibers.

4. Count bundles of fibers as one fiber unless individual fibers can be identified by observing both ends of a fiber.
5. Count enough graticule fields to yield 100 fibers. Count a minimum of 20 fields. Stop at 100 fields regardless of fiber count.

b. B Rules

NOTE: The B Rules are preferred analytically because of their demonstrated ability to improve the reproducibility of fiber counts [5].

1. Count only ends of fibers. Each fiber must be longer than 5 µm and less than 3 µm diameter.
2. Count only ends of fibers with a length-to-width ratio equal to or greater than 5:1.
3. Count each fiber end which falls within the graticule area as one end, provided that the fiber meets rules b.1 and b.2.
4. Count visibly free ends which meet rules b.1 and b.2 when the fiber appears to be attached to another particle, regardless of the size of the other particle.
5. Count the free ends of fibers emanating from large clumps and bundles up to a maximum of 10 ends (5 fibers), provided that each segment meets rules b.1 and b.2.
6. Count enough graticule fields to yield 200 ends. Count a minimum of 20 fields. Stop at 100 fields, regardless of the fiber count.
7. Divide the total end count by 2 to yield fiber count.

NOTE: Split fibers will normally be counted as more than two ends if the free ends meet the rules b.1. and b.2.

20. Start counting from one end of the filter and progress along a radial line to the other end, shift either up or down on the filter and continue in the reverse direction [10]. Select fields randomly by looking away from the eyepiece briefly while advancing the mechanical stage. When an agglomerate covers ca. 1/6 or more of the field of view, reject the field and select another. Do not report rejected fields in the number of total fields counted.

NOTE: When counting a field, continuously scan a range of focal planes by moving the fine focus knob to detect very fine fibers which have become embedded in the filter. The small-diameter fibers will be very faint but are an important contribution to the total count.

CALCULATIONS:

21. Calculate and report fiber density on the filter, E (fibers/mm^2), by dividing the total fiber count, F, minus the mean field blank count, B, by the number of fields, n, and the field area, A_f (0.00785 mm^2 for a properly calibrated Walton-Beckett graticule):

$$E = \frac{(F - B)}{(n)(A_f)}, \text{ fibers/mm}^2.$$

22. Calculate the concentration, C (fibers/mL), of fibers in the air volume sampled, V (L), using the effective collection area of the filter, A_c (385 mm^2 for a 25-mm filter):

$$C = \frac{(E)(A_c)}{V \cdot 10^3}.$$

NOTE: Periodically check and adjust the value of A_c, if necessary.

EVALUATION OF METHOD:

This method is a revision of NIOSH Method P&CAM 239 [1,3,4]. A summary of the revisions is as follows:

A. Sampling

The change from a 37-mm to a 25-mm filter size was incorporated to improve sensitivity and reduce problems associated with non-uniform fiber loading reported on the 37-mm filters [10]. The change in flow rates allows for 2 m^3 full-shift samples to be taken, providing that the filter is not overloaded with non-fibrous particulates. The collection efficiency of the sampler is not affected by changes in flow rate in the range 0.5 to 16 L/min [8].

B. Sample Preparation Technique

The acetone vapor-triacetin preparation technique has been incorporated in the method as a faster, more permanent mounting technique than the dimethyl phthalate/diethyl oxalate method of P&CAM 239 [1,3,4,11].

C. Measurement

1. The inclusion of the Walton-Beckett graticule in the method was made to standardize the field area observed through the eyepiece [6,11].
2. The introduction of the HSE/NPL test slide was made to standardize microscope optics for sensitivity to fiber diameter [7,11].
3. A recent international collaborative study involved 16 laboratories using prepared slides from the asbestos, cement, milling, mining, textile, and friction material industries [5]. The relative levels of count by different counting rules were:

Sample Type	Number of Samples	Aspect Ratio > 3:1		Aspect Ratio > 5:1	
		AIA	Mod. CRS*	AIA	Mod. CRS*
Mining	10	100	127	74	92
Milling	10	100	112	84	95
Asbestos Cement	14	100	146	90	137
Textile Chrysotile	10	100	109	89	99
Friction Material	10	100	130	87	116
Others (Insulation, Amosite)	6	100	127	92	118
TOTAL: 60 MEAN:		100	125	86	110

*Arithmetic means of counts made by different laboratories relative to the AIA counts.

The modified CRS (NIOSH B) Rules were found to be more precise than the AIA (NIOSH A)* Rules. The ranges of relative standard deviations (s_r) which varied with sample type and laboratory were:

	s_r		
	Intralaboratory	Interlaboratory	Overall
AIA (NIOSH A Rules)*	0.12 to 0.40	0.27 to 0.85	0.46
Modified CRS (NIOSH B Rules)	0.11 to 0.29	0.20 to 0.35	0.25

*Under AIA rules, only fibers having a diameter less than 3 μm are counted and fibers attached to particles larger than 3 μm are not counted. NIOSH A Rules are otherwise similar to the AIA rules.

The B Rules have also been favorably received by analysts as less ambiguous and simpler to use; these rules also showed the least bias relative to AIA rules in the collaborative study. An independent NIOSH laboratory study using amosite fibers reported a relative standard deviation, including within- and between-sample

variability, of 0.157 for the B Rules [12]. Adding an estimated sampling pump error, s_r, of 0.05 [13] to the within-sample variability in this study results in an estimate of overall precision, s_r, of 0.102 for the B Rules.

4. Because of past inaccuracies associated with low fiber counts, the minimum loading has been increased to 100 fibers/mm^2 filter area (80 fibers total count). This level yields an overall s_r = 0.13, as indicated in Figure 3 (revised) of P&CAM 239 [3,4] which corresponds to a measurement s_r = 0.12 after removal of pump error [13]. Similarly, at the maximum count of 100 fibers, overall s_r = 0.115 and measurement s_r = 0.10 are obtained.

D. Evaluation of the method using the A and B counting rules will proceed on a continuing basis through the NIOSH Proficiency Analytical Testing (PAT) Program. The new PAT reporting form allows for reporting of results by either set of rules as of January, 1984.

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FORMULA: F

M.W.: 18.998

FLUORIDES, aerosol and gas

METHOD: 7902
ISSUED: 2/15/84

OSHA: 2.5 mg/m³ (fluorides); 3 ppm (HF)
NIOSH: 2.5 mg/m³ (fluorides) [1];
5 mg/m³/15 min (HF) [2]
ACGIH: 2.5 mg/m³ (fluorides); 3 ppm (HF)

PROPERTIES: HF: liquid; BP 19.5 °C;
Fluoride salts liberate HF in presence of acids

SYNONYMS: sodium fluoride (CAS #7681-49-4), hydrogen fluoride, hydrofluoric acid (CAS #7664-39-3), cryolite, sodium hexafluoroaluminate.

SAMPLING

SAMPLER: FILTER + TREATED FILTER
(0.8-µm cellulose ester membrane followed by a Na_2CO_3-treated cellulose pad)

FLOW RATE: 1 to 2 L/min

VOL-MIN: 20 L @ 2.5 mg/m³
-MAX: 800 L @ 2.5 mg/m³

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: none identified

OVERALL PRECISION (s_r): not evaluated

MEASUREMENT

TECHNIQUE: ION-SPECIFIC ELECTRODE

ANALYTE: fluoride ion (F^-)

FILTER (particulate F^-): fuse in NaOH; dissolve in 50 mL water + TISAB

TREATED FILTER (gaseous F^-): extract in 50 mL water + TISAB

CALIBRATION: standard F^- solutions in TISAB

RANGE: 0.03 to 1.2 mg F^- per sample

ESTIMATED LOD: 3 µg F^- per sample [11]

PRECISION (s_r): 0.017 [3]

APPLICABILITY: The working range is 0.1 to 5 mg/m³ for a 250-L air sample. Water-soluble particulates may be extracted by the procedure for gaseous fluorides. Insoluble particulates require fusion. In samples containing cryolite ore, aluminum is sufficiently concentrated to give erroneous fluoride concentrations [5]. The method applies to mining samples; insecticide, Al reduction, ceramic, glass etching, electroplating, semi-conductor, and fluorochemical industries; and water treatment samples.

INTERFERENCES: Hydroxide ion greater than 1/10 of the fluoride level will interfere positively. Addition of TISAB and pH 5.5 will compensate. Addition of 0.1 M cyclohexylene diamine tetraacetic acid (CDTA) will suppress up to 500 µg/mL Fe^{+3} and 90 µg/mL Si^{+4}. Al^{+3} gives a negative interference ; concentrations > 8 µg/mL cannot be suppressed [10].

OTHER METHODS: This method combines and replaces P&CAM 212 [4], P&CAM 117 [5] and S176 [6]. Method 7903 (inorganic acids) is an alternate method for HF.

REAGENTS:

1. Sodium carbonate (Na_2CO_3).
2. Glycerol.
3. Potassium chloride (KCl).
4. Sodium acetate ($NaC_2H_3O_2 \cdot 3H_2O$).
5. Cyclohexylene diamine tetraacetic acid (CDTA).
6. Hydrochloric acid, 1:1 (v/v).
7. Sodium fluoride (NaF).
8. Deionized (DI) water.
9. Alkaline fixative solution. Dissolve 25 g Na_2CO_3 in deionized water. Add 20 mL glycerol. Dilute to 1 L.
10. Total ionic strength activity buffer (TISAB), pH 5.5. Dissolve 37 g KCl, 68 g sodium acetate and 36 g CDTA in H_2O. Adjust to pH 5.5 ± 0.2 with 1:1 HCl. Dilute to 1 L.
11. Calibration stock solution, 100 µg F^-/mL. Dissolve 0.2211 g NaF (dried at 105 °C for 2 hrs) in DI H_2O; dilute to 1 L.
12. Sodium hydroxide, 20% (w/v). Dissolve 200 g NaOH in DI water to make 1 L solution.

EQUIPMENT:

1. Sampler: Two filter cassettes in line.
   a. Moisten 37-mm cellulose backup pad with 0.8 mL alkaline fixative solution. Dry at 105 °C for 30 to 45 min. Mount in 37-mm filter cassette holder. Seal with shrinkable band or tape.
   b. Assemble sampler: (1) cassette containing 37-mm, 0.8-µm cellulose ester membrane filter and untreated backup pad connected by PVC tubing to (2) cassette containing impregnated backup pad.
2. Personal sampling pump, 1 to 2 L/min, with flexible connecting tubing.
3. Crucibles, nickel or Inconel, 20-mL.
4. Bunsen or Meaker burner.
5. Tripod.
6. Triangle, ceramic-covered.
7. Volumetric flasks, 50- and 100-mL.
8. Pipets, appropriate sizes for standards.
9. Beakers, plastic, 100-mL.
10. Magnetic stirrer.
11. PTFE-coated stirring bars.
12. Fluoride ion selective electrode (ISE), combination or with calomel-type reference electrode.
13. pH/ion meter with millivolt readout.
14. pH electrode.

SPECIAL PRECAUTIONS: Fluorides are extremely corrosive to skin, eyes and mucous membranes [1,2]. Perform all fusions in fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 2 L/min for a total sample size of 20 to 800 L. Do not exceed 2 mg total dust loading on the filter.
3. Separate the two parts of the sampler for shipment.

SAMPLE PREPARATION:

4. Cellulose ester membrane filter (particulate fluoride).
   a. Transfer the membrane filter to a crucible containing 5 mL 20% NaOH.
   b. Evaporate to dryness.
   c. Heat residue to fusion temperature, 1 to 2 min, cool and dissolve in ca. 5 mL DI H_2O.
   d. Transfer sample into 100-mL plastic beaker
   e. Rinse crucible with 25 mL of TISAB then with a few drops of 1:1 HCl.
   f. Adjust to pH 5.5 ± 0.2 using 1:1 HCl.
   g. Transfer to 50-mL volumetric flask; dilute to volume with DI H_2O.

5. Alkaline-impregnated backup pad (gaseous fluoride).
   a. Open cassettes and transfer impregnated cellulose pads to 100-mL plastic beakers.
   b. Add 25 mL TISAB and 25 mL DI H_2O.
   c. Soak pad for 30 min with sufficient stirring to reduce it to pulp.

CALIBRATION AND QUALITY CONTROL:

6. Calibrate daily with at least five working standards over the range 0.003 to 1.2 mg F^- per sample.
   a. Add known amounts of calibration stock solution to 25 mL TISAB and 5 mL 20% NaOH (particulate fluoride) or 25 mL TISAB (gaseous fluoride) in 100-mL beakers.
   b. Adjust pH to 5.5 $\pm$ 0.2 with 1:1 HCl.
   c. Transfer to 50-mL volumetric flasks. Dilute to the mark with DI water.
      NOTE: Working standards are stable at least one month in polyethylene bottles at 4 °C.
   d. Analyze together with samples and blanks (steps 7 through 10).
   e. Prepare separate calibration graphs (mV vs. log F^- concentration) for particulate and gaseous fluorides.
      NOTE: Calibration curve is not linear below 0.1 µg/mL or above 25 µg/mL. Additional standards are necessary for fluoride concentrations in these ranges.

MEASUREMENT:

7. Bring sample and standard solutions to room temperature.
   NOTE: Samples and standards must be at same temperature (within $\pm$ 2 °C) for accurate results.
8. Pour ca. 20 mL of each solution into plastic beakers.
9. Add magnetic stir bar, insert electrodes and gently stir on magnetic stirrer.
10. Record potential (mV) after 2 min.
    NOTE: If measured concentration of F^- is above the linear range of the calibration graph, dilute the sample with fluoride standards matrix, reanalyze and use the appropriate dilution factor in calculations.

CALCULATIONS:

11. Using the proper calibration graph (particulate or gaseous), convert potential (mV) to solution fluoride concentration, C_s (µg/mL), in the solution volume, V_s (mL).
12. Calculate the concentration of fluoride, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{C_s V_s}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Measurement precision, s_r, in the range 0.055 to 0.22 mg HF per sample averaged 0.017 with average recovery 100.0% [3]. Analytical results on field samples report detection limits of 3 µg per sample for both gaseous and particulate fluorides. Reported collection ranges for gaseous fluoride was 4 to 61 µg per sample; for particulates, 4 to 410 µg per sample [11].

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[11] UBTL Reports, NIOSH Sequence #2454, 2703, 3117 and 3366 (unpublished).

METHOD REVISED BY: Mary Ellen Cassinelli, NIOSH/DPSE.

FORMULA: $H_2C=O$; CH_2O

M.W.: 30.03

FORMALDEHYDE

METHOD: 2502
ISSUED: 2/15/84

OSHA: 3 ppm; C 5 ppm; peak 10 ppm
NIOSH: lowest feasible level [1]
ACGIH: 1 ppm; STEL 2 ppm
(1 ppm = 1.23 mg/m³ @ NTP)

PROPERTIES: gas; BP -19.5 °C;
vapor density 1.067 (air = 1);
explosive range 7 to 73% v/v in air

SYNONYMS: methanal; CAS #50-00-0; Formalin (aqueous 30 to 50% w/v HCHO).

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(2-(benzylamino)ethanol on Chromosorb 102 or XAD-2, 120 mg/60 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 1 L @ 3 ppm
-MAX: 15 L

SHIPMENT: routine

SAMPLE STABILITY: 4 weeks @ 25 °C

BLANKS: 2 media blanks and 2 field blanks per set of 10; 6 unopened tubes for DE determination (same lot as samples)

ACCURACY

RANGE STUDIED: 0.55 to 4.7 mg/m³ [2]

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.061 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: 3-benzyloxazolidine

DESORPTION: 2 mL isooctane; ultrasonic bath 45 min or shake 4 hr

INJECTION VOLUME: 1 µL, splitless; split vent time 30 sec

TEMPERATURE-INJECTION: 210 °C
-DETECTOR: 220 °C
-COLUMN: 70 °C for 1 min; 10 °C/min; hold @ 200 °C for 11.5 min

GASES-CARRIER: He, 100 kPa, ca 0.5 cm³/min; makeup flow, 29 cm³/min

COLUMN: fused silica capillary, 25 m x 0.2 mm; Carbowax 20M

CALIBRATION: solutions of 3-benzyloxazolidine in isooctane

RANGE: 4 to 60 µg per sample

ESTIMATED LOD: 1 µg per sample [3]

PRECISION (s_r): 0.055 [2]

APPLICABILITY: The working range is 0.3 to 5 mg/m³ (0.25 to 4 ppm) for a 12-L air sample.

INTERFERENCES: Phenol has a retention time close to that of 3-benzyloxazolidine but is baseline-resolved. Acid mists may inactivate the sorbent leading to inefficient collection of formaldehyde.

OTHER METHODS: This method was formerly designated P&CAM 354 [4]. It has improved sample stability and ease of personal sampling compared to Methods 3500 and 3501. Method 3500 (chromotropic acid) is the most sensitive.

REAGENTS:

1. Water, distilled, deionized.
2. Eluent: Isooctane, chromatographic grade, containing 0.025% (v/v) hexadecane or other suitable internal standard.
3. Formalin solution, 37%.*
4. Sulfuric acid, 0.02 N.
5. Sodium hydroxide, 0.01 N.
6. Sodium sulfite, 1.13 M.
7. Toluene, distilled in glass.
8. 2-(benzylamino)ethanol, distilled, 100 to 130 °C at 130 Pa (1 mm Hg).
9. 3-Benzyloxazolidine (see Appendix).
10. Formaldehyde stock solution, 1 mg/mL (see Appendix). Stable at least 3 months.
11. Helium, purified.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 10 cm x 4 mm ID, containing a 120-mg front section and 60-mg backup section of 2-(benzylamino)ethanol on either Chromosorb 102 or XAD 2. Sorbent sections are retained and separated by small plugs of glass wool. Pressure drop ca. 0.2 kPa (0.8 inch water) at 50 cm^3/min airflow. Tubes are commercially available or may be prepared according to the Appendix.
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, capillary column capability, FID, integrator (page 2502-1).
4. Vials, 4-mL, with plastic screw caps.
5. Ultrasonic bath or mechanical shaker.
6. Pipettes, volumetric, 1-, 5- and 10-mL, with pipet bulb.
7. Flasks, volumetric, 10-mL and 1-L.
8. Burettes, 50-mL.
9. pH meter.
10. Disposable pipettes, 2-mL.
11. Syringe, 10-µL, readable to 0.1 µL.

SPECIAL PRECAUTIONS: Formaldehyde is viewed as a potential occupational carcinogen by NIOSH [1].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.05 L/min for a total sample size of 1 to 15 L.

   NOTE 1: Sampling rate is limited by the speed of reaction of formaldehyde with the sorbent coating. At 0.10 L/min, appreciable formaldehyde (ca. 25%) is found on the backup section, possibly invalidating the sample. At higher flow rates, formaldehyde concentrations will be grossly underestimated.

   NOTE 2: The presence of acid mists or gases may interfere indirectly by reacting with the 2-(benzylamino)ethanol to form amine salts which are not reactive with formaldehyde. If a sufficient amount of the 2-(benzylamino)ethanol is consumed by the acid, formaldehyde concentrations found with the method may be lower than the true concentrations.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Score each sampler with a file in back of the rear sorbent section.
6. Break sampler at score line. Remove and place glass wool plug and rear sorbent section in a vial.
7. Transfer front section with the remaining glass wool plugs to a vial.

8. Add 2.0 mL eluent to each vial. Screw cap tightly onto each vial.
9. Agitate vials in an ultrasonic bath for at least 45 min or in a shaker for 4 hr.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least five working standards.
    a. Add known amounts of 3-benzyloxazolidine to eluent in 10-mL volumetric flasks and dilute to the mark.
       NOTE: Prepare standard solutions for splitless injection in the range 1 to 50 µg/mL; for split injection, in the range 1 to 400 µg/mL.
    b. Analyze together with samples and blanks (steps 13 and 14).
    c. Prepare calibration graph (ratio of peak area or height of analyte to peak area or height of internal standard vs. µg 3-benzyloxazolidine) for the injection technique used.
11. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 10). Prepare three tubes at each of five levels plus three media blanks.
    a. Remove and discard back sorbent section of a media blank sampler.
    b. Inject a known amount of formaldehyde stock solution directly onto front sorbent section with a microliter syringe.
    c. Cap the tube. Allow to stand overnight.
    d. Desorb (steps 5 through 9) and analyze together with working standards (steps 13 and 14).
    e. Prepare a graph of DE vs. µg 3-benzyloxazolidine recovered.
12. Analyze three quality control blind spiked and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

13. Set gas chromatograph to conditions given on page 2502-1. Set air and hydrogen flows on the flame ionization detector to manufacturer's specifications. Inject 1-µL sample aliquot via the splitless injection technique. t_r = 11.5 min for these conditions.
    NOTE: If sample amount of 3-benzyloxazolidine overloads the column (> 50 ng/µL for 0.2 mm ID column), either dilute sample with eluent or inject via split injection technique, reanalyze, and apply appropriate volume correction factor in calculations. Column overloading is indicated by a plateau on the calibration graph at high concentrations. If split injection is required, the following conditions are typical:

Column temperature program:	150 °C for 7 min; 10 °C/min; hold at 200 °C
Split flow rate:	10 cm^3/min He
Retention time:	5.9 min

14. Measure peak area or height. Divide the peak area or height of analyte by the peak area or height of internal standard on the same chromatogram.

CALCULATIONS

15. Determine the mass, µg (corrected for DE) of 3-benzyloxazolidine found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE 1: If $W_b > W_f/10$, report breakthrough and possible sample loss.
    NOTE 2: A blank level of 1 to 7 µg HCHO is typical. Measure sufficient media blanks (at least 2 per 10 samples) to determine a representative mean value.

16. Multiply by the desorption volume (2 mL) and the conversion factor (0.184) from 3-benzyloxazolidine to formaldehyde to calculate concentration, C, of formaldehyde in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 2\ mL \cdot 0.184}{V},\ mg/m^3.$$

EVALUATION OF METHOD

Side-by-side comparisons of this method using laboratory-prepared samplers with a 2,4-dinitrophenylhydrazine-coated silica gel tube method [5] were done in a formaldehyde production facility. Means of the two methods were not significantly different [6]. Lab testing with spiked samplers and atmospheres generated by syringe pump/air dilution [2]; verified by 2,4-dinitrophenylhydrazine-coated silica gel tubes [5]. Breakthrough volume of laboratory-prepared samplers (80% RH, 6 mg HCHO/m^3, 0.05 L/min) was greater than 16 L; DE (10.5, 37.5, 76.0 µg per sample) = 99%; recovery after storage (0.85 µg per sample) = 94.3% after two weeks at 25 °C; precision and accuracy as given on page 2502-1 (24 samples). When acetaldehyde was present as a cocontaminant, 5% breakthrough volume was 16 L (80% RH, 10 mg HCHO/m^3, 10 mg acetaldehyde/m^3, 0.05 L/min). Sampling rate influences reaction of formaldehyde with the sorbent coating. Rates above 0.05 L/min give low results with laboratory-prepared samplers.

In a breakthrough study done using commercially-available tubes, the breakthrough volume was found to be greater than 73 L at 8.7 mg/m^3 and greater than 58 L at 28 mg/m^3 of formaldehyde. These atmospheres were sampled at 0.078 L/min.

An atmosphere of 0.36 mg/m^3 formaldehyde, as determined by P&CAM 125 [7], was sampled with sets of six tubes at ca. 0.08 L/min for 70 min, 286 min and 482 min. The average amount indicated by these tubes was 0.32 mg/m^3 with the relative standard deviation less than 10% in all cases. The tube loadings for these sampling periods were 1.6, 6.3 and 10.8 ug. This information indicates that concentrations as low as 0.1 mg/m^3 should be measurable with a sampling rate of 0.08 L/min and a sampling time of 8 hrs.

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METHOD WRITTEN BY: Eugene R. Kennedy, Ph.D., and Robert H. Hill, Jr., Ph.D., NIOSH/DPSE.

APPENDIX:

SAMPLING TUBE PREPARATION

Extract Chromosorb 102 or XAD-2 with a 50/50 (v/v) mixture of acetone/methylene chloride in a soxhlet apparatus for 4 hrs using a 30-min cycle time. Vacuum dry [1 mm Hg (133 Pa)] the sorbent at ambient temperature overnight. To a slurry of the dried, extracted sorbent (10 g in 100 mL toluene), add 1 g distilled 2-(benzylamino)ethanol in 10 mL toluene. Allow to stand for 1 hr with occasional swirling. Remove the solvent by rotary evaporation and vacuum dry [1 mm Hg (133 Pa)] at ambient temperature overnight. For each batch of the coated sorbent, desorb several 100-mg portions with isooctane and analyze. If the background is greater than 7 µg 3-benzyloxazolidine/100 mg coated sorbent, discard the batch.

PREPARATION OF 3-BENZYLOXAZOLIDINE

Add a solution of 1.51 g (10 mmole) 2-(benzylamino)ethanol in 10 mL toluene dropwise to a solution of 1 mL 37% formalin (0.37 g formaldehyde, 12.3 mmole) in 25 mL toluene. Stir 1 hr. Remove the solvent at reduced pressure by rotary evaporation. The product is a yellow viscous oil. Vacuum distill at 58 to 62 °C at 1 mm Hg (133 Pa); yields 3-benzyloxazolidine as a clear, colorless oil, stable at room temperature for several months in a closed vial.

PREPARATION AND STANDARDIZATION OF FORMALDEHYDE STOCK SOLUTION (ca. 1 mg/mL)

Dilute 2.7 mL 37% formalin solution to 1 L with distilled, deionized water. This solution is stable at least three months. Standardize as follows:

Place 5.0 mL 1.13 M sodium sulfite solution in a beaker, stirred with a magnetic stirrer. Adjust pH to between 7 and 9 with base or acid. Record the pH. Add 10.0 mL stock formaldehyde solution. The pH should now be about 12. Titrate the solution back to its original pH with 0.02 N sulfuric acid (1 mL acid = 0.600 mg HCHO; about 17 mL acid needed). If the endpoint pH is overrun, back titrate to the endpoint with 0.01 N sodium hydroxide. Calculate the concentration, C_S (mg/mL), of the formaldehyde stock solution:

$$C_S = \frac{30.0 \cdot [(N_a \cdot V_a) - (N_b \cdot V_b)]}{V_S}$$

where: 30.0 = 30.0 g/equivalent of formaldehyde
N_a = normality of sulfuric acid
V_a = volume of sulfuric acid (mL) used for titration
N_b = normality of NaOH
V_b = volume of NaOH (mL) used for back titration
V_S = volume of HCHO stock solution (10.0 mL).

FORMULA: $H_2C{=}O$; CH_2O

M.W. = 30.03

FORMALDEHYDE

METHOD: 3500
ISSUED: 2/15/84

OSHA: 3 ppm; C 5 ppm; P 10 ppm
NIOSH: lowest feasible level [1]
ACGIH: C 2 ppm
(1 ppm = 1.23 mg/m³ @ NTP

PROPERTIES: gas; BP -19.5 °C;
vapor density 1.067 (air = 1.00);
explosive range 7 to 73 % v/v in air

SYNONYMS: methanal; CAS #50-00-0; formalin (aqueous 30 to 50% w/v HCHO).

SAMPLING

SAMPLER: FILTER + IMPINGERS
(1-µm PTFE membrane and 2 impingers, each with 20 mL 1% sodium bisulfite solution)

FLOW RATE: 0.2 to 1 L/min

VOL-MIN: 2 L @ 1 ppm
-MAX: 100 L

SHIPMENT: transfer samples to bottles before shipping

SAMPLE STABILITY: 30 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 100 to 600 µg per sample [2]

BIAS: none identified

OVERALL PRECISION (s_r): 0.09 [2]

MEASUREMENT

TECHNIQUE: VISIBLE ABSORPTION SPECTROPHOTOMETRY

ANALYTE: formaldehyde

SAMPLE WORKUP: note liquid volume; remove 4-mL aliquot

ANALYSIS: color development (chromotropic acid + sulfuric acid); absorbance @ 580 nm

CALIBRATION: solutions of formaldehyde in distilled water

RANGE: 2 to 40 µg per sample

ESTIMATED LOD: 0.5 µg per sample [2,3]

PRECISION (s_r): 0.03 [2]

APPLICABILITY: The working range is 0.02 to 0.4 ppm (0.025 to 0.5 mg/m³) for an 80-L air sample. This is the most sensitive formaldehyde method in the NIOSH Manual of Analytical Methods and is able to measure ceiling levels as low as 0.1 ppm (15-L sample). It is also preferred for the determination of formaldehyde in area samples at all concentrations due to its simplicity.

INTERFERENCES: Phenols, in 8-fold excess over formaldehyde, produce a -10% to -20% bias [4]. Ethanol and higher M.W. alcohols, olefins, aromatic hydrocarbons [5] and cyclohexanone also produce small negative interferences [4]. Little interference is seen from other aldehydes [4].

OTHER METHODS: This method was originally adapted from the Intersociety Committee [6] and designated P&CAM 125 [4]. For personal samples or where interferences to this method are present, use Method 2502.

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REAGENTS:

1. Chromotropic acid, 1%. Dilute 0.10 g 4,5-dihydroxy-2,7-naphthalene disulfonic acid disodium salt to 10 mL with distilled water. Filter. Store in brown bottle. Prepare fresh weekly.
2. Sulfuric acid, 96%.*
3. Formaldehyde stock solution, 1 mg/mL (See APPENDIX).
4. Formalin solution, 37%.*
5. Distilled, deionized water.
6. Sulfuric acid, 0.02 N, aqueous.
7. Sodium hydroxide, 0.01 N, aqueous.
8. Sodium sulfite, 1.13 M, aqueous.
9. Sodium bisulfite, 1%. Dissolve 1 g in distilled water. Dilute to 100 mL. Prepare fresh weekly.

*See Special Precautions.

EQUIPMENT:

1. Sampler: 37-mm filter cassette with 37-mm polytetrafluoroethylene (PTFE) membrane filter, 1- to 3-μm pore size followed by two midget impingers; inert, flexible tubing for cassette-to-impinger connection.
2. Personal sampling pump, 0.2 to 1 L/min, with flexible connecting tubing.
3. Bottles, screw-cap Nalgene CPE, 50-mL.
4. Spectrophotometer, visible, 580 nm.
5. Volumetric pipettes, 0.1-, 0.5-, 1-, 4-, 5-, 6- and 10-mL; 1-, 2- and 5-mL, graduated in 0.1-mL units, with pipet bulb.
6. Volumetric flasks, 10- and 100-mL, and 1-L.
7. Burets, 50-mL.
8. pH meter.
9. Pipettes, 2-mL, disposable, with pipet bulb.
10. Spectrophotometer cuvettes, 1-cm.
11. Flasks, glass-stoppered, 25-mL.
12. Graduated cylinder, 25-mL.
13. Waterbath at 95 °C.
14. Magnetic stirrer.
15. Beaker, 50-mL.

SPECIAL PRECAUTIONS: Sulfuric acid is extremely corrosive; handle while wearing acid-resistant gloves, apron and full face shield with goggles.

Formaldehyde is viewed as a potential carcinogen by NIOSH [1] and should be handled in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Fill the two impingers for each sample with 20 mL 1% sodium bisulfite solution. Make cassette-to-impinger and impinger-to-sampling pump conections with flexible, inert tubing. Insert a second filter/cassette assembly in line between the sampler and sampling pump to trap any liquid which might splash over from the impingers during sampling.
3. Sample at an accurately known flow rate between 0.2 and 1 L/min for a total sample size of 2 to 100 L.
4. Transfer the contents of the impingers to separate polyethylene bottles for shipping.

SAMPLE PREPARATION:

5. Transfer each impinger solution to a clean, dry 25-mL graduated cylinder. Note volume of solution from front impinger, V_f (mL), backup impinger, V_b (mL), and blank impinger, V_B (mL).
6. Pipette 4-mL aliquots from each sample solution into 25-mL glass-stoppered flasks.
   NOTE: Adjust aliquot size to contain between 2 and 20 μg formaldehyde for optimum absorbance.

CALIBRATION AND QUALITY CONTROL:

7. Prepare a calibration stock solution by dilution of 1 mL of 1 mg/mL formaldehyde stock solution to 100 mL with 1% sodium bisulfite solution.
8. Pipet, e.g., 0, 0.1, 0.3, 0.5, 0.7, 1.0 and 2.0 mL calibration stock solution into 25-mL glass-stoppered flasks.
9. Add 1% sodium bisulfite solution to bring the volume of each working standard to 4 mL.
   NOTE: These working standards contain approximately 0, 1, 3, 5, 7, 10, and 20 µg formaldehyde. Use the exact values based on standardization of the formaldehyde stock solution.
10. Analyze together with samples and blanks (steps 12 through 15.
11. Prepare calibration graph (absorbance vs. µg formaldehyde/4 mL).

MEASUREMENT:

12. Add 0.1 mL 1% chromotropic acid to the flask and mix.
13. Add 6 mL conc. H_2SO_4 slowly to the flask. Replace the stopper gently. Gently swirl the solution to mix.
    CAUTION: Exothermic reaction.
14. Heat the solution to 95 °C for 15 min. Cool the solution to room temperature.
    NOTE: Use caution due to the corrosive nature of hot sulfuric acid and the possible pressure buildup within the flask.
15. Read sample absorbance at 580 nm in a 1-cm cuvette.
    NOTE: If absorbance is greater than the highest standard, take a smaller aliquot, dilute to 4 mL with 1% sodium bisulfite solution, and analyze.

CALCULATIONS:

16. Calculate the mass, µg, of formaldehyde in each front impinger (M_f), back impinger (M_b) and average blank impinger (M_B). Use the appropriate aliquot factor (e.g., 4 mL aliquot/original volume from step 6) and the total sample volume noted in step 5.
    NOTE: Discard the sample if the mass found in the backup impinger exceeds 1/3 the mass found in the front impinger. Collection efficiency is <0.95 for each impinger.
17. Calculate the concentration, C (mg/m^3), of formaldehyde in the air volume sampled, V (L):

$$C = \frac{M_f + M_b - 2M_B}{V}, \ mg/m^3$$

EVALUATION OF THE METHOD:

The method was checked for reproducibility by having three different analysts in three different laboratories analyze standard samples containing between 1 and 20 µg formaldehyde. The results agreed within ± 5% [6]. This method was independently compared with the 2,4,-dinitrophenylhydrazine-coated silica gel method of Beasley et al. over the range of 0.8 to 2.2 ppm formaldehyde [8] and was found to give approximately 25% lower concentrations.In another study comparing this method, P&CAM 318 [7], and the method of Beasley, et al., all three methods were found to be statistically equivalent under laboratory test conditions and loadings from 8.2 to 22.4 µg per sample of formaldehyde [9].

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[1] NIOSH Current Intelligence Bulletin 34, "Formaldehyde: Evidence of Carcinogenicity," U.S. Department of Health and Human Services, Publ. (NIOSH) (NIOSH) Publication No. 81-111 (1981).
[2] Formaldehyde, No. S327 Failure Report, NIOSH/OSHA Standards Completion Program Contract Report (1976).
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METHOD REVISED BY: Eugene R. Kennedy, Ph.D., NIOSH/DPSE.

APPENDIX:

PREPARATION AND STANDARDIZATION OF FORMALDEHYDE STOCK SOLUTION (ca. 1 mg/mL)
Dilute 2.7 mL 37% formalin solution to 1 L with distilled, deionized water. Standardize as follows:

Place 5.0 mL 1.13 M sodium sulfite solution in a 50-mL beaker, stirred with a magnetic stirrer. Adjust pH to between 7 and 9 with base or acid. Record the pH. Pipet 10.0 mL stock formaldehyde solution into the beaker. The pH should now be about 12. Titrate the solution back to its original pH with 0.02 N sulfuric acid. (1 mL of 0.02 N sulfuric acid = 0.600 mg HCHO; about 17 mL acid needed.) Calculate the concentration, C_S (mg/mL), of the stock formaldehyde solution:

$$C_S = \frac{30.0 \cdot [(N_a \cdot V_a) - (N_b \cdot V_b)]}{V_S}$$

where: 30.0 = 30.0 g/equivalent of formaldehyde
N_a = normality of sulfuric acid
V_a = volume of acid (mL) used for titration
N_b = normality of NaOH
V_b = volume of NaOH (mL) used for back titration
V_S = volume of HCHO stock solution (10.0 mL).

FORMULA: $H_2C=O$; CH_2O

M.W. = 30.03

FORMALDEHYDE

METHOD: 3501
ISSUED: 2/15/84

OSHA: 3 ppm; C 5 ppm; P 10 ppm/30 min
NIOSH: lowest feasible level [1]
ACGIH: C 2 ppm
(1 ppm = 1.23 mg/m³ @ NTP)

PROPERTIES: gas; BP -19.5 °C;
vapor density 1.067 (air = 1);
explosive range 7 to 73% v/v in air

SYNONYMS: methanal; CAS #50-00-0; Formalin (aqueous 30 to 50% w/v HCHO).

SAMPLING

SAMPLER: LIQUID IN BUBBLER
(midget bubbler, 15 mL Girard T reagent)

FLOW RATE: 0.05 to 0.2 L/min

VOL-MIN: 6 L
-MAX: 18 L

SHIPMENT: seal bubblers to prevent leakage before shipping

SAMPLE STABILITY: 1 week @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 33 to 133 µg per sample [5]

BIAS: not significant [5]

OVERALL PRECISION (s_r): 0.052 (TWA) [5];
0.058 (Ceiling) [5]

MEASUREMENT

TECHNIQUE: POLAROGRAPHY

ANALYTE: formaldehyde-Girard T derivative

SAMPLE PREPARATION: note volume of sample; transfer to dry vessel with ca. 0.3 mL Hg

POLAGRAPHY: sampled DC; 1 sec drop time, scan; -0.7 to -1.3 V vs. saturated calomel electrode @ 5 mV/sec

CALIBRATION: solutions of formaldehyde in distilled water

RANGE: 33 to 133 µg per sample

ESTIMATED LOD: 6 µg per sample

PRECISION (s_r): 0.021 [5]

APPLICABILITY: In attempts at validation of P&CAM 125 [4], a sample stability problem was noted [3]. This method was found to overcome this problem. Being a bubbler method, it is best suited to area sampling. The method has sufficient sensitivity to make peak measurements over the range of 4.6 to 19.8 ppm.

INTERFERENCES: Other volatile aldehydes such as acrolein, crotonaldehyde and benzaldehyde and products diffusing out of polyvinyl chloride tubing may cause significant interference.

OTHER METHODS: This method was formerly designated S327 [2]. For personal samples or where interferences in this method are present, Method 2502 (formerly P&CAM 354), is preferred. Method 3500 (chromotropic acid) is more sensitive, although cumbersome for personal samples.

REAGENTS:

1. Citric acid, reagent grade.
2. Disodium hydrogen phosphate, reagent grade.
3. Girard T reagent, reagent grade.
4. Buffered Girard T reagent (See APPENDIX).
5. Triton X-100, 0.075%. Dilute 0.75 mL Triton X-100 to 1 L with distilled water.
6. Formalin solution, 37%.*
7. Distilled, deionized water.
8. Sulfuric acid, 0.02 N.
9. Sodium hydroxide solution, 0.01 N.
10. Sodium sulfite solution, 1.13 M.
11. Formaldehyde stock solution*, 6.6 mg/mL (See APPENDIX). Stable at least three months.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass midget bubblers.
2. Personal sampling pump, 0.05 to 0.2 L/min, with flexible connecting tubing.
3. Volumetric flasks, 1-L, 100-mL.
4. China marker.
5. Burettes, 50-mL.
6. Polarograph, capable of DC or DC sampled polarography with reference to a saturated colomel electrode.
7. Syringes, volumetric, 1-, 10-, 25- and 50-µL.
8. Pipets, volumetric, 0.3-, 0.75-, 1-, 2-, 5-, 10-, 15- and 20-mL, graduated in 0.1-mL increments.
9. pH meter.
10. Pipets, disposable, 2-mL.
11. Graduated cylinder, 25-mL.

SPECIAL PRECAUTIONS: Formaldehyde is viewed as a potential occupational carcinogen by NIOSH [1].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Fill the bubbler with 15 mL buffered Girard T reagent solution using a 15-mL pipet. Mark the initial liquid level in the bubbler with a China marker.
3. Make bubbler-to-sampling pump conections with flexible inert tubing. Insert a glass wool trap between bubbler and personal sampling pump to prevent splashover.
4. Sample at 0.2 L/min for 30 min (6 L) for peak measurements or at, e.g., 0.1 L/min for 1 to 3 hrs (6 to 18 L) for TWA measurements. Do not exceed a sample volume of 18 L, in order to maintain an 80-fold molar excess of the Girard T reagent over the total amount of formaldehyde sampled.

SAMPLE PREPARATION:

5. Tap the bubbler stem lightly against the bubbler body to drain the contents into the body. If necessary, bring samples up to the 15-mL volume mark with distilled water. Swirl the bubbler to mix.
6. Transfer solution to a clean, dry polarographic cell which contains a small amount of mercury (0.3 mL).

CALIBRATION AND QUALITY CONTROL:

7. Add aliquots of the standardized formaldehyde stock solution (ca. 6.6 mg/mL) to 15-mL volumetric flasks using volumetric syringes and bring to volume with the buffered Girard T reagent. Prepare six working standards to cover the range of 6 to 220 µg per sample.
8. Analyze these standards as directed in steps 6, and 10 through 13.
9. Prepare calibration graph (µg formaldehyde/15 mL vs. diffusion current).

MEASUREMENT:

10. Place the cell on the polarograph and purge the sample for 5 min with oxygen-free nitrogen at a flow rate of 200 mL/min.
11. Analyze the sample with sampled DC polarography using conditions given on page 3501-1 of the method.
12. Rinse electrodes with distilled water between samples.
13. Measure diffusion current from the reduction of the formaldehyde-Girard T reagent derivative.
    NOTE: The half-wave potential of the formaldehyde- Girard T reagent derivative is -0.99 V vs. saturated calomel electrode.

CALCULATIONS:

14. Read the µg formaldehyde/15 mL of Girard T reagent found in the sample (W) and the average blank (B) from the calibration graph.
15. Calculate the concentration of formaldehyde in the air volume sampled, V (L):

$$C = \frac{(W - B)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S327 was validated under the joint NIOSH/OSHA Standards Completion Program September 2, 1977 [5,6].

REFERENCES:

[1] NIOSH Current Intelligence Bulletin 34, "Formaldehyde: Evidence of Carcinogenicity," U.S. Department of Health and Human Services, Publ. (NIOSH) 81-111 (1981).
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[6] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY: Eugene R. Kennedy, Ph.D., NIOSH/DPSE; S327 validated under NIOSH Contract 210-76-0123.

APPENDIX:

PREPARATION AND STANDARDIZATION OF FORMALDEHYDE STOCK SOLUTION (ca. 6.6 mg/mL)
Dilute 17.9 mL 37% formalin solution to 1 L with distilled, deionized water. Standardize as follows:

Place 5.0 mL 1.13 M sodium sulfite solution in a beaker. Stir the solution using a magnetic stirrer. Measure the pH, which should be in the range between 7 and 9. Adjust to this range with base or acid if necessary. Record the pH value. Pipet 2.0 mL stock formaldehyde solution into the beaker. The pH should now be about 12. Titrate the solution back to its original pH with 0.02 N sulfuric acid. Approximately 20 mL of acid will be needed. One mL 0.02 N sulfuric acid is equivalent to 0.600 mg of formaldehyde. Calculate the concentration, C_S (mg/mL), of the stock formaldehyde solution:

$$C_S = \frac{30.0 \cdot [(N_a \cdot V_a) - (N_b \cdot V_b)]}{V_S}$$

where: C_S = concentration of the formaldehyde stock solution in g/L
30.0 = 30.0 g/equivalent of formaldehyde
N_a = normality of sulfuric acid
V_a = volume of acid (mL) used for titration
N_b = normality of NaOH
V_b = volume of NaOH (mL) for back titration
V_S = volume of formaldehyde solution used in titration (2.0 mL).

BUFFERED GIRARD T REAGENT:
Dissolve 13.3 g disodium hydrogen phosphate, 10.8 g citric acid, 3.93 g Girard T reagent in a 1-L volumetric flask. Add 6.6 mL Triton X-100 solution and dilute to 1 L with distilled water. The pH of the resulting solution should be 4.5.

BIOLOGICAL SAMPLES

3503-1

NIOSH MANUAL OF ANALYTICAL METHODS

THIRD EDITION

Peter M. Eller, Ph.D., CIH
Editor

VOLUME 2

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Public Health Service
Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Physical Sciences and Engineering
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DHHS (NIOSH) Publication No. 84-100

2503-1-a

FORMULA: H_2NNH_2; H_4N_2

M.W.: 32.05

HYDRAZINE

METHOD: 3503
ISSUED: 2/15/84

OSHA: 1 ppm (skin)
NIOSH: 0.04 mg/m³ [1]
ACGIH: 0.1 ppm (skin; suspect carcinogen)
(1 ppm = 1.31 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.004 g/mL @ 25 °C;
BP 113.5 °C; MP 2 °C;
VP 14.4 mm Hg @ 25 °C (1.92 kPa;
18,900 ppm)
flash point (open cup) 38 to 52 °C

SYNONYMS: diamide; diamine; CAS #302-01-2.

SAMPLING

SAMPLER: BUBBLER
(0.1 M HCl)

FLOW RATE: 0.2 to 1.0 L/min

VOL-MIN: 7 L @ 1.3 mg/m³
-MAX: 100 L

SHIPMENT: routine

SAMPLE STABILITY: ≥ 6 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.59 to 3.4 mg/m³ [2]
(91-L samples)

BIAS: not determined

OVERALL PRECISION (s_r): 0.094 [2]

MEASUREMENT

TECHNIQUE: VISIBLE ABSORPTION SPECTROPHOTOMETRY

ANALYTE: quinoid derivative of
p-dimethylaminobenzaldazine [3]

COMPLEXATION: p-dimethylaminobenzaldehyde;
stand 30 min; acetic acid

FINAL VOLUME: 625 mL

WAVELENGTH: 480 nm

CALIBRATION: hydrazine in methanol

RANGE: 9 to 400 µg per sample

ESTIMATED LOD: 0.9 µg per sample

PRECISION (s_r): 0.031 [2]

APPLICABILITY: The working ranges are 0.09 to 4.0 mg/m³ for 100-L air samples and 0.6 to 27 mg/m³ for 15-L air samples. This method is applicable to hydrazine vapor. It has not been tested with aerosol forms. The free base cannot be distinguished from salts, such as hydrazine monohydrochloride and hydrazine sulfate, which are aerosols.

INTERFERENCES: Methylhydrazine is an interference. Other hydrazines may interfere.

OTHER METHODS: This method is a modification of and replaces Method S237 [4]. Method P&CAM 248 is a gas chromatographic method which can be used for quantitation of hydrazine or substituted hydrazines [5]. Methods S143, S149 and S160 utilize a nonspecific colorimetric method for substituted hydrazines [6].

REAGENTS:

1. Hydrochloric acid, 0.1 M. Dilute 8.6 mL conc. HCl to 1 L with distilled water.
2. Methanol, reagent grade.*
3. Calibration stock solution, 1.0 mg/mL. Dissolve 0.10 mL hydrazine* in methanol to make 100 mL solution.
4. Solution of p-dimethylamino-benzaldehyde in methanol, 0.168 M. Dissolve 12.5 g p-dimethylamino-benzaldehyde in methanol to make 500 mL solution.
5. Glacial acetic acid.*
6. Sodium hydroxide solution, 1.8 M. Dissolve 7.2 g NaOH in distilled water to make 100 mL solution.

*See Special Precautions.

EQUIPMENT:

1. Sampler: midget bubbler, glass, with 15 mL 0.1 M HCl.
2. Glass tube, 5 cm x 6 mm ID, packed loosely with glass wool.
3. Personal sampling pump, 0.2 to 1 L/min, with flexible connecting tubing.
4. Vials, 20-mL, with PTFE-lined screw caps.
5. Spectrophotometer set at 480 nm, with matched cuvettes, glass, 1-cm path length.
6. Volumetric flasks, 25-, 50-, 100- and 500-mL and 1-L.
7. Pipets, 1-, 2-, 10- and 15-mL, with pipet bulb.
8. Syringe, 10-µL, readable to 0.1 µL.
9. Syringe, 50-µL, readable to 1 µL.
10. pH paper.

SPECIAL PRECAUTIONS: Hydrazine is carcinogenic, toxic, and flammable, and can be absorbed through the skin [1].

Acetic acid and methanol are flammable. Wear gloves, handle compounds in a well-ventilated fume cabinet, avoid inhalation of vapors, and protect compounds from sparks and flames.

SAMPLING:

1. Connect the outlet of the sampler and the inlet of the pump to a tube packed with glass wool to protect the pump from splashover.
2. Calibrate the personal sampling pump with sampler in line.
3. Sample at 0.2 to 1.0 L/min for a sample size of 7 to 100 L.
4. Transfer the solution from the bubbler to a glass vial, rinsing both the bubbler stem and body with 1-mL portions of 0.1 M HCl. Cap the vial securely for shipment.

SAMPLE PREPARATION:

5. Transfer bubbler solution to a 50-mL volumetric flask.
6. Rinse vial with 1 mL 0.1 M HCl, and add rinse to the flask.
7. Add 1.8 M NaOH (ca. 1 mL) to make the solution neutral or slightly alkaline to pH paper.
8. Immediately add 10 mL 0.168 M p-dimethylaminobenzaldehyde solution. Agitate the mixture and allow to stand 30 min.
9. Bring volume of solution to 50 mL with glacial acetic acid.
10. Dilute 2 mL of the solution to 25 mL with glacial acetic acid.
11. Prepare field blanks and media blanks according to steps 4 through 10.

CALIBRATION AND QUALITY CONTROL:

12. Calibrate daily with a blank and six working standards over the range 1 to 400 µg hydrazine per sample.
    a. Add aliquots of calibration stock solution to 18 mL 0.1 M HCl in 50-mL volumetric flasks. Designate one flask as a blank and do not add hydrazine to that flask.
    b. Process the working standards according to steps 7 through 10.
    c. Determine absorbance for each solution (steps 13 and 14).
    d. Prepare calibration graph (absorbance vs. µg hydrazine).

MEASUREMENT:

13. Set up the spectrophotometer according to manufacturer's instructions. Place blank solution (from step 12.a) into reference cuvette.
14. Determine absorbance of solution at 480 nm.

CALCULATIONS:

15. Determine the quantities of hydrazine in the sample, W (µg), and average media blank, B (µg), from the calibration graph.
16. Calculate the concentration, C (mg/m^3), of hydrazine in the air volume sampled, V (L):

$$C = \frac{W - B}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

This method is based on Method S237 using 15 mL of 0.1 M HCl for sampling instead of 10 mL. Method S237 was evaluated with controlled atmospheres of hydrazine [2]. Overall precision (s_r) was 0.094 (18 samples, pooled) for 91-L samples at 0.59 to 3.4 mg/m^3. Concentrations of hydrazine in controlled atmospheres were not verified by an independent method. Average collection efficiency at 0.9 L/min for six bubblers was 0.997 at 3.4 mg/m^3. Average recoveries from HCl solution were 1.03, 0.98 and 1.01 at the 60.7-, 121- and 243-µg levels of hydrazine, respectively. The precision (s_r) = 0.031 (18 samples, pooled). Samples at the 121-µg level were stable during storage in 0.1 M HCl for six days at room temperature.

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[1] Criteria for a Recommended Standard...Occupational Exposure to Hydrazines,U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-172 (1978).
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[5] Ibid, V. 1, P&CAM 248, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[6] Ibid, V. 3, S143, S149, S160.

METHOD REVISED BY: Samuel P. Tucker, Ph.D., NIOSH/DPSE; S237 developed under NIOSH Contract CDC-99-74-45.

FORMULA: Table 1

M.W.: Table 1

HYDROCARBONS, BP 36 – 126 °C

METHOD: 1500
ISSUED: 2/15/84

OSHA, NIOSH, ACGIH: Table 2

PROPERTIES: Table 1

COMPOUNDS:	benzene	n-heptane	n-octane
(Synonyms	cyclohexane	n-hexane	n-pentane
in Table 1)	cyclohexene	methylcyclohexane	toluene

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal,
100 mg/50 mg)

FLOW RATE, VOLUME: Table 3

SHIPMENT: no special precautions

SAMPLE STABILITY: at least 2 weeks

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: desirable, 1 to 10 mL; ship in separate containers from samples

ACCURACY

RANGE STUDIED,
BIAS and OVERALL PRECISION (s_r): Table 3

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTES: hydrocarbons listed above

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 250 °C
-COLUMN: see step 11

CARRIER GAS: N_2 or He, 25 mL/min

COLUMN: glass, 3.0 m x 2 mm, 20% SP-2100 on 80/100 mesh Supelcoport

CALIBRATION: analytes in CS_2

RANGE AND PRECISION (s_r): Table 4

ESTIMATED LOD: 0.001 to 0.01 mg per sample with capillary column [1]

APPLICABILITY: This method is intended for determining the OSHA-regulated hydrocarbons included within the boiling point range of n-pentane through n-octane. It may be used for simultaneous measurements; however, interactions between analytes may reduce breakthrough volumes and change desorption efficiencies.

INTERFERENCES: At high humidity, breakthrough volumes may be reduced by as much as 50%. Other volatile organic solvents, e.g., alcohols, ketones, ethers, and halogenated hydrocarbons, are likely interferences. If interference is suspected, use a more polar column or change column temperature.

OTHER METHODS: This method is based on and supercedes Methods P&CAM 127, benzene and toluene [2]; S28, cyclohexane [3]; S82, cyclohexene [3]; S89, heptane [3]; S90, hexane [3]; S94, methylcyclohexane [3]; S311, benzene [4]; S343, toluene [4]; S378, octane [4]; and S379, pentane [4]. For benzene or toluene in complex mixture of alkanes ($\leq C_{10}$), Method 1501 (aromatic hydrocarbons) is more selective.

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REAGENTS:

1. Eluent: Carbon disulfide*, chromatographic quality with (optional) suitable internal standard.
2. Analytes, reagent grade.*
3. Nitrogen or helium, purified.
4. Hydrogen, prepurified.
5. Air, filtered.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg, back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section, and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1500-1).
4. Vials, glass, 1-mL, with PTFE-lined caps.
5. Pipet, 1-mL, with pipet bulb.
6. Syringes, 5-, 10-, 25- and 100-µL.
7. Volumetric flasks, 10-mL

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and extremely flammable (flash point = -30 °C); benzene is a suspect carcinogen. Prepare samples and standards in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min (0.01 to 0.05 L/min for n-pentane) for a total sample size as shown in Table 3.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial immediately.
7. Allow to stand at least 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the appropriate range (ca. 0.01 to 10 mg analyte per sample; see Table 4).
   a. Add known amounts of analyte to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11, 12 and 13).
   c. Prepare calibration graph (peak area of analyte vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of analyte directly onto front sorbent section with a microliter syringe.

c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11, 12 and 13).
e. Prepare a graph of DE vs. mg analyte recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control. Check for possible contamination during shipment of field samples by comparing results from field blanks and media blanks.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1500-1. Select appropriate column temperature:

Substance	Approximate Retention Time (min), at Indicated Column Temperature			
	40 °C	70 °C	100 °C	Programmed[a]
n-pentane	2.2	1.2		1.8
solvent (CS_2)	3.0	1.6		2.4
n-hexane	5.1	2.2		3.5
benzene[b]	7.7	3.2		4.5
cyclohexane[b]	8.4	3.4		4.7
cyclohexene	9.5	3.8		4.9
n-heptane	12	4.3		5.4
methylcyclohexane	14	5.2	2.2	5.9
toluene	17	6.5	2.6	6.5
n-octane	19	8.7	3.2	7.1

[a]Temperature program: 50 °C for 2 min, then 15 °C/min to 150 °C, 2-min final hold.
[b]Not completely resolved.

NOTE: Alternatively, column and temperature may be taken from Table 4.

12. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
13. Measure peak area.

CALCULATIONS:

14. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:
Precisions and biases (Table 3) were determined by analyzing generated atmospheres containing one-half, one, and two times the OSHA standard. Generated concentrations were independently verified. Breakthrough capacities were determined in dry air. Storage stability was not assessed. Measurement precisions (Table 4) were determined by spiking sampling media with amounts corresponding to one-half, one, and two times the OSHA standard for nominal air volumes. Desorption efficiencies for spiked samplers containing only one compound exceeded 75%. Reference [12] provides more specific information.

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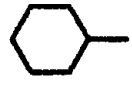
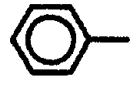
[1] User check, UBTL, NIOSH Sequence #4213-L (unpublished, January 31, 1984).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 127 U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 2, S28, S82, S89, S90, S94, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[4] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3., S311, S343, S378, S379, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[5] R. D. Driesbach, "Physical Properties of Chemical Compounds"; Advances in Chemistry Series, No. 15; American Chemical Society, Washington (1955).
[6] R. D. Driesbach, "Physical Properties of Chemical Compounds - II"; Advances in Chemistry Series, No. 22; American Chemical Society, Washington (1959).
[7] Code of Federal Regulations; Title 29 (Labor), Parts 1900 to 1910; U.S. Government Printing Office, Washington, (1980); 29 CFR 1910.1000.
[8] Update Criteria and Recommendations for a Revised Benzene Standard, U.S. Department of Health, Education, and Welfare, (August 1976).
[9] Criteria for a Recommended Standard....Occupational Exposure to Alkanes (C5-C8), U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-151 (1977).
[10] Criteria for a Recommended Standard....Occupational Exposure to Toluene, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 73-11023 (1973).
[11] TLVs--Threshold Limit Values for Chemical Substances and physical Agents in the Work Environment with Intended Changes for 1983-84, ACGIH, Cincinnati, OH (1983).
[12] Documentation of the NIOSH Validation Tests, S28, S82, S89, S90, S94, S311, S343, S378, S379, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).

METHOD REVISED BY: R. Alan Lunsford, Ph.D., and Julie R. Okenfuss; based on results of NIOSH Contract CDC-99-74-45.

Table 1. Synonyms, formula, molecular weight, properties.

Name Synonyms	Structure	Empirical Formula	Molecular Weight	Boiling Point (°C)	Vapor Pressure @ 25 °C (mm Hg)	Vapor Pressure @ 25 °C (kPa)	Density @ 20 °C (g/mL)
benzene[a] CAS #71-43-2		C_6H_6	78.11	80.1	95.2	12.7	0.879
cyclohexane[a] CAS #110-82-7 hexahydrobenzene hexamethylene		C_6H_{12}	84.16	80.7	97.6	13.0	0.779
cyclohexene[a] CAS #110-83-8 tetrahydrobenzene		C_6H_{10}	82.15	83.0	88.8	11.8	0.811
n-heptane[b] CAS #142-82-5		C_7H_{16}	100.21	98.4	45.8	6.1	0.684
n-hexane[b] CAS #110-54-3		C_6H_{14}	86.18	68.7	151.3	20.2	0.659
methylcyclohexane[a] CAS #108-87-2		C_7H_{14}	98.19	100.9	46.3	6.2	0.769
n-octane[b] CAS #111-65-9		C_8H_{18}	114.23	125.7	14.0	1.9	0.703
n-pentane[b] CAS #109-66-0		C_5H_{12}	72.15	36.1	512.5	68.3	0.626
toluene[a] CAS #108-88-3 methylbenzene		C_7H_8	92.14	110.6	28.4	3.8	0.867

[a]Properties from [5].
[b]Properties from [6].

Table 2. Permissible exposure limits, ppm [7-11].

Substance	OSHA TWA	OSHA C	OSHA Peak	NIOSH TWA	NIOSH C	ACGIH TLV	ACGIH STEL	mg/m³ per ppm @ NTP
benzene*	10	25	50[b]	1		10	25	3.19
cyclohexane	300					300	375	3.44
cyclohexene	300					300		3.36
n-heptane	500			85	440	400	500	4.10
n-hexane[a]	500			100	510	50		3.52
methylcyclohexane	500					400	500	4.01
n-octane	500			75	385	300	375	4.67
n-pentane	1000			120	610	600	750	2.95
toluene	200	300	500[b]	100	200[c]	100	150 (skin)	3.77

[a]The ACGIH recommendation for other hexane isomers is: TLV 500, STEL 1000.
[b]Maximum duration 10 min in 8 hr.
[c]10-min sample.
*ACGIH: suspect carcinogen

Table 3. Sampling flowrate[a], volume, capacity, range, overall bias and precision [2-4, 12].

Substance	Sampling Flowrate (L/min)	Sampling Volume (L) VOL-NOM	Sampling Volume (L) VOL-MAX[b]	Breakthrough Volume at Concentration (L)	Breakthrough Volume at Concentration (mg/m³)	Range at VOL-NOM (mg/m³)	Overall Bias (%)	Overall Precision (s_r)
benzene	≤0.20	2[c]	30	>45	149.1	41.5 - 165	0.8	0.059
cyclohexane	≤0.20	2.5	5	7.6	1650	510 - 2010	5.4	0.060[d]
cyclohexene	≤0.20	5	7	10.4	2002	510 - 2030	9.0	0.073
n-heptane	≤0.20	4	4	6.1	4060	968 - 4060	-6.5	0.056
n-hexane	≤0.20	4	4	5.9	3679	877 - 3679	-3.8	0.062
methylcyclohexane	≤0.20	4	4	6.1	3941	940 - 3941	5.5	0.052
n-octane	≤0.20	4	4	6.5	4612	1050 - 4403	-5.2	0.060
n-pentane	≤0.05	2	2	3.1	5640	1476 - 6190	-9.7	0.055
toluene	≤0.20	2[c]	8	11.9	2294	548 - 2190	3.8	0.052

[a]Minimum recommended flow is 0.01 L/min.
[b]Approximately two-thirds the breakthrough volume.
[c]10-min sample.
[d]Corrected value, calculated from data in [12].

Table 4. Measurement range, precision, and chromatographic conditions [2-4,12].

	Measurement[a]		Carrier		Column Parameters[b]			
Substance	Range (mg)	Precision (s_r)	Gas	Flow (mL/min)	t (°C)	Length (m)	Dia-meter (mm)	Packing[c]
benzene	0.09-0.35	0.036	N_2	50	115	0.9	3.2	A
cyclohexane	1.3 - 5.3[d]	0.024	N_2	50	210	1.2	6.4	B
cyclohexene	2.4 - 9.7[d]	0.021	N_2	50	205	1.2	6.4	B
n-heptane	4.08-16.3	0.016	He	30	80	3.0	3.2	C
n-hexane	3.56-14.5	0.014	He	30	52	6.1	3.2	D
methylcyclohexane	3.98-16.1	0.012	He	30	55	6.1	3.2	D
n-octane	4.75-18.9	0.009	He	30	52	6.1	3.2	D
n-pentane	2.98-11.8	0.014	He	30	52	6.1	3.2	D
toluene	1.13-4.51	0.011	N_2	50	155	0.9	3.2	B

[a]Injection volume, 5.0 µL; desorption volume, 1.0 mL, except cyclohexane and cyclohexene, 0.5 mL.

[b]All columns stainless steel. Diameter is outside dimension.

[c]A, 50/80 mesh Porapak P; B, 50/80 mesh Porapak Q; C, 10% OV-101 on 100/120 mesh Supelcoport; D, 10% FFAP on 80/100 mesh Chromosorb W AW-DMCS.

[d]Corrected value, calculated from data in [12].

FORMULA: Table 1

M.W.: Table 1

HYDROCARBONS, AROMATIC

METHOD: 1501
ISSUED: 2/15/84

OSHA, NIOSH, ACGIH: Table 2

PROPERTIES: Table 1

COMPOUNDS: (Synonyms in Table 1)	benzene	cumene	α-methylstyrene	styrene	vinyltoluene
	p-tert-butyltoluene	ethylbenzene	naphthalene	toluene	xylene

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal,
100 mg/50 mg)

FLOW RATE, VOLUME: Table 3

SHIPMENT: no special precautions

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: desirable, 1 to 10 mL; ship in separate containers from samples

ACCURACY

RANGE STUDIED,
BIAS and OVERALL PRECISION (s_r): Table 3

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTES: hydrocarbons listed above

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 225 °C
-DETECTOR: 225 °C
-COLUMN: see step 11

CARRIER GAS: N_2 or He, 25 mL/min

COLUMN: glass, 3.0 m x 2 mm, 10% OV-275 on 100/120 mesh Chromosorb W-AW or equivalent

CALIBRATION: analytes in CS_2

RANGE AND PRECISION (s_r): Table 4

ESTIMATED LOD: 0.001 to 0.01 mg per sample with capillary column [1]

APPLICABILITY: This method is for peak, ceiling and TWA determinations of aromatic hydrocarbons It may be used for simultaneous measurements, though there is the possibility that interactions between analytes may reduce the breakthrough volumes and change desorption efficiencies.

INTERFERENCES: Use of the recommended column will prevent interference by alkanes ($\leq C_{10}$). Under conditions of high humidity, the breakthrough volumes may be reduced by as much as 50%. Other volatile organic solvents, e.g., alcohols, ketones, ethers and halogenated hydrocarbons, are possible interferences. If interference is suspected, use a less polar column or change column temperature.

OTHER METHODS: This method is based on and supercedes Methods P&CAM 127, benzene, styrene, toluene and xylene [2]; S311, benzene [4]; S22, p-tert-butyltoluene [3]; S23, cumene [3]; S29, ethylbenzene [3]; S26, α-methylstyrene [3]; S292, naphthalene [4]; S30, styrene [3]; S343, toluene [4]; S25, vinyltoluene [3]; S318, xylene [4].

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REAGENTS:

1. Eluent: Carbon disulfide*, chromatographic quality containing (optional) suitable internal standard.
2. Analytes, reagent grade*
3. Nitrogen or helium, purified
4. Hydrogen, prepurified.
5. Air, filtered.
6. Naphthalene calibration stock solution, 0.40 g/mL in CS_2.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg, back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pumps, 0.01 to 1 L/min (Table 3), with flexible connecting tubing.
3. Gas chromatograph, FID, integrator, and column (page 1501-1).
4. Vials, glass, 1-mL, with PTFE-lined caps.
5. Pipet, 1-mL, and pipet bulb.
6. Syringes, 5-, 10-, 25- and 100-µL.
7. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and extremely flammable (flash point = -30 °C); benzene is a suspect carcinogen. Prepare samples and standards in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min (to 1 L/min for naphthalene or styrene) for a total sample size as shown in Table 3.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial immediately.
7. Allow to stand at least 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the appropriate range (ca. 0.01 to 10 mg analyte per sample; see Table 4).
   a. Add known amounts of analyte (calibration stock solution for naphthalene) to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11, 12 and 13).
   c. Prepare calibration graph (peak area of analyte vs. mg analyte).

9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of analyte (calibration stock solution for naphthalene) directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11, 12 and 13).
   e. Prepare a graph of DE vs. mg analyte recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1501-1. Select appropriate column temperature:

	Approximate Retention Time (min), at Indicated Column Temperature			
Substance[a]	50 °C	100 °C	150 °C	Programmed[b]
benzene	2.5			2.5
toluene	4.3	1.1		4.2
xylene (para)	7.0	1.4		5.2
ethylbenzene	7.0	1.4		5.5
xylene (meta)	7.2	1.5		5.6
cumene	8.3	1.6		6.0
xylene (ortho)	10	1.9		6.5
styrene	16	2.6		7.6
α-methylstyrene		3.2	1.0	8.1
vinyltoluene (meta)		3.8	1.2	8.5
naphthalene		25	4.3	12

[a]Data not available for p-tert-butyltoluene and p-vinyltoluene.
[b]Temperature program: 50 °C for 3 min, then 15 °C/min to 200 °C.

NOTE: Alternatively, column and temperature may be taken from Table 4.

12. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
13. Measure peak area.

CALCULATIONS:

14. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.

15. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

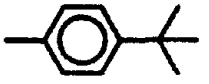
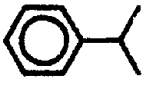
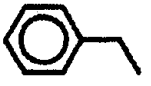
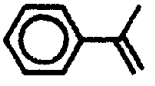
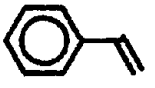
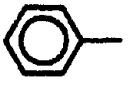
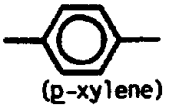
Precisions and biases listed in Table 3 were determined by analyzing generated atmospheres containing one-half, one, and two times the OSHA standard. Generated concentrations were independently verified. Breakthrough capacities were determined in dry air. Storage stability was not assessed. Measurement precisions given in Table 4 were determined by spiking sampling media with amounts corresponding to one-half, one, and two times the OSHA standard for nominal air volumes. Desorption efficiencies for spiked samplers containing only one compound exceeded 75%. Reference [12] provides more specific information.

REFERENCES:

[1] User check, UBTL, NIOSH Sequence #4121-S (unpublished, December 7, 1983).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 127, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[3] Ibid, V. 2, S22, S23, S25, S26, S29, S30, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[4] Ibid, V. 3, S292, S311, S318, S343, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[5] R. D. Dreisbach. "Physical Properties of Chemical Compounds"; Advances in Chemistry Series, No. 15; American Chemical Society, Washington (1955).
[6] Code of Federal Regulations; Title 29 (Labor), Parts 1900 to 1910; U.S. Government Printing Office, Washington (1980); 29 CFR 1910.1000.
[7] Update Criteria and Recommendations for a Revised Benzene Standard, U.S. Department of Health, Education, and Welfare, (August 1976).
[8] Criteria for a Recommended Standard....Occupational Exposure to Toluene, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 73-11023 (1973).
[9] Criteria for a Recommended Standard....Occupational Exposure to Xylene, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 75-168 (1975).
[10] TLVs - Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment with Intended Changes for 1983-84, ACGIH, Cincinnati, OH (1983).
[11] Criteria for a Recommended Standard...Occupational Exposure to Styrene, U.S. Department of Health and Human Services, Publ. (NIOSH) 83-119 (1983).
[12] Documentation of the NIOSH Validation Tests, S22, S23, S25, S26, S29, S30, S292, S311, S318, S343, U.S. Department of Health, Education, and Welfare; Publ. (NIOSH) 77-185 (1977).

METHOD REVISED BY: R. Alan Lunsford, Ph.D., and Julie R. Okenfuss; based on results of NIOSH Contract CDC-99-74-45.

Table 1. Synonyms, formula, molecular weight, properties [5].

Name/Synonyms	Structure	Empirical Formula	Molecular Weight	Boiling Point (°C)	Vapor Pressure @ 25 °C (mm Hg)	Vapor Pressure @ 25 °C (kPa)	Density @ 20 °C (g/mL)
benzene CAS #71-43-2		C_6H_6	78.11	80.1	95.2	12.7	0.879
p-tert-butyltoluene CAS #98-51-1 1-tert-butyl-4-methylbenzene		$C_{11}H_{16}$	148.25	192.8	0.7	0.09	0.861
cumene CAS #98-82-8 isopropylbenzene		C_9H_{12}	120.20	152.4	4.7	0.62	0.862
ethylbenzene CAS #100-41-4		C_8H_{10}	106.17	136.2	9.6	1.28	0.867
α-methylstyrene CAS #98-83-9 isopropenylbenzene (1-methylethenyl)-benzene		C_9H_{10}	118.18	165.4	2.5	0.33	0.911
naphthalene CAS #91-20-3		$C_{10}H_8$	128.18	80.2[a]	0.2	0.03	1.025
styrene CAS #100-42-5 vinylbenzene		C_8H_8	104.15	145.2	6.1	0.81	0.906
toluene CAS #108-88-3 methylbenzene		C_7H_8	92.14	110.6	28.4	3.79	0.867
vinyltoluene[b] CAS #25013-15-4 methylstyrene methylvinylbenzene	 (p-vinyltoluene)	C_9H_{10}	118.18 (meta) (para) (ortho)	167.7 171.6 172.8 169.8	1.6 1.9 1.8 1.8	0.22 0.26 0.24 0.24	0.898 0.911 0.911 0.904
xylene[c] CAS #1330-20-7 dimethylbenzene	 (p-xylene)	C_8H_{10}	106.17 (ortho) (meta) (para)	 144.4 139.1 138.4	 6.7 8.4 8.8	 0.89 1.12 1.18	 0.880 0.864 0.861

[a]Melting point.
[b]Commercial mixture of meta and para isomers.
[c]Mixture of isomers.

Table 2. Permissible exposure limits, ppm [6-11].

Substance	OSHA TWA	OSHA C	OSHA Peak	NIOSH TWA	NIOSH C	ACGIH TLV	ACGIH STEL	mg/m³ per ppm
benzene	10	25	50[a]	1		10**	25**	3.19
p-tert-butyltoluene	10					10	20	6.06
cumene	50	(skin)				50	75 (skin)	4.91
ethylbenzene	100					100	125	4.34
α-methylstyrene		100				50	100	4.83
naphthalene	10					10	15	5.24
styrene	100	200	600[b]	50	100	50	100	4.26
toluene	200	300	500[a]	100	200*	100	150 (skin)	3.77
vinyltoluene	100					50	100	4.83
xylene	100			100	200*	100	150	4.34

[a]Maximum duration 10 min in 8 hr.
[b]Maximum duration 5 min in any 3 hr.
**ACGIH: suspect carcinogen [10].
* 10-min sample.

Table 3. Sampling flowrate[a], volume, capacity, range, overall bias and precision [3,4,12].

Substance	Sampling Flowrate (L/min)	Sampling Volume (L) VOL-NOM	Sampling Volume (L) VOL-MAX[b]	Breakthrough Volume @ Concentration (L)	Breakthrough Volume @ Concentration (mg/m³)	Range at VOL-NOM (mg/m³)	Overall Bias (%)	Overall Precision (s_r)
benzene	≤0.20	2[c]	30	>45	149	42- 165	0.8	0.059
p-tert-butyltoluene	≤0.20	10	29	44	112	29- 119	-10.4	0.071[d]
cumene	≤0.20	10	30	>45	480	120- 480	4.6	0.059
ethylbenzene	≤0.20	10	24	35	917	222- 884	-8.1	0.089[d]
α-methylstyrene	≤0.20	3[f]	30	>45	940	236- 943	-10.8	0.061[d]
naphthalene[e]	≤1.0	200	200	>240	81	19- 83	-0.5	0.055
styrene	≤1.0	5[g]	14	21	1710	426-1710	-10.7	0.058[d]
toluene	≤0.20	2[c]	8	12	2294	548-2190	3.8	0.052
vinyltoluene	≤0.20	10	24	36	952	256- 970	-9.5	0.061[d]
xylene	≤0.20	12	23	35	870	218- 870	-2.1	0.060

[a]Minimum recommended flow is 0.01 L/min.
[b]Approximately two-thirds the breakthrough volume, except for naphthalene.
[c]10-min sample.
[d]Corrected value, calculated from data in Reference 12.
[e]Naphthalene shows poor desorption efficiency at low loading; 100-L minimum volume is recommended.
[f]15-min sample.
[g]5-min sample.

Table 4. Measurement range, precision and conditions[a] [3,4,12].

Substance	Desorption Volume (mL)	Measurement Range (mg)	Measurement Precision (s_r)	Carrier Flow (mL/min)	Column Parameters[b] t (°C)	Column Parameters[b] Length (m)	Column Parameters[b] Packing[c]
benzene	1.0	0.09- 0.35	0.036	50	115	0.9	A
p-tert-butyltoluene	0.5	0.27- 1.09	0.021[d]	50	115	3.0	B
cumene	0.5	0.86- 3.46	0.010	50	99	3.0	B
ethylbenzene	0.5	2.17- 8.67	0.010	50	85	3.0	B
α-methylstyrene	0.5	0.69- 3.57	0.011	50	115	3.0	B
naphthalene	1.0	4.96-19.7	0.019	30	125	3.0	C
styrene	0.5	2.17- 8.49	0.013[d]	50	109	3.0	B
toluene	1.0	1.13- 4.51	0.011	50	155	0.9	D
vinyltoluene	0.5	2.41- 9.64	0.008	50	120	3.0	B
xylene	1.0	2.60-10.4	0.010	50	180	0.9	D

[a]Injection volume, 5.0 µL; nitrogen carrier gas.
[b]All columns stainless steel, 3.2 mm outside diameter.
[c]A, 50/80 mesh Porapak P; B, 10% FFAP on 80/100 mesh Chromosorb W AW-DMCS; C, 10% OV-101 on 100/120 mesh Supelcoport; D, 50/80 mesh Porapak Q.
[d]Corrected value, calculated from data in [12].

FORMULA: Table 1

M.W.: Table 1

HYDROCARBONS, HALOGENATED

METHOD: 1003
ISSUED: 2/14/84

COMPOUNDS: (synonyms in Table 1)
benzyl chloride
bromoform
carbon tetrachloride
chlorobenzene
chlorobromomethane
chloroform
o-dichlorobenzene
p-dichlorobenzene
1,1-dichloroethane
1,2-dichloroethylene
ethylene dichloride
hexachloroethane
methylchloroform
propylene dichloride

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: Table 2
-MAX: Table 2

SHIPMENT: routine

SAMPLE STABILITY: at least 1 week @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD [1]

BIAS: not significant [1]

OVERALL PRECISION (s_r): see EVALUATION OF METHOD [1]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 1 mL CS_2, stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURES: Table 2

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: Table 2; alternates are SP-2100, SP-2100 with 0.1% Carbowax 1500 or DB-1 fused silica capillary column

CALIBRATION: solutions of analyte in CS_2 with internal standard, if necessary

RANGE: Table 2

ESTIMATED LOD: 0.01 mg per sample [2]

PRECISION (s_r): see EVALUATION OF METHOD [1]

APPLICABILITY: This method uses a simple desorption and can be used for simultaneous analysis of two or more substances suspected to be present by changing the gas chromatographic conditions (i.e., temperature programmed). High humidity during sampling will prevent organic vapors from being trapped efficiently on the sorbent and greatly decreases breakthrough volume.

INTERFERENCES: None identified. The chromatographic column or separation conditions may be changed to circumvent interference problems.

OTHER METHODS: This method combines and replaces Methods P&CAM 127 [3]; S95, S101, S110, S113, S114, S115, S122, S123 and S133 [4]; and S135, S281, S314, S328 and S351 [5].

Preceding page blank

REAGENTS:

1. Eluent: Carbon disulfide,* chromatographic quality, containing 0.1% (v/v) toluene, ethyl benzene or other suitable internal standard (see Table 2).
2. Analyte, reagent grade.
3. Calibration stock solutions.
   a. benzyl chloride, 10 mg/mL in n-heptane.
   b. bromoform, 10 mg/mL in n-hexane.
   c. o-dichlorobenzene, 200 mg/mL in carbon disulfide.
   d. p-dichlorobenzene, 300 mg/mL in acetone.
4. Nitrogen or helium, purified.
5. Hydrogen, prepurified.
6. Air, filtered.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (see Table 1).
4. Vials, 2-mL, glass, PTFE-lined crimp caps.
5. Volumetric flasks, 10-mL.
6. Syringe, 10-µL, readable to 0.1 µL.
7. Pipet, 1-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of as shown in Table 2.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the appropriate range (Table 2).
   a. Add known amounts of analyte or calibration stock solution to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.

a. Remove and discard back sorbent section of a media blank sampler.
b. Inject a known amount of analyte or calibration stock solution directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg analyte recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1003-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Laboratory testing was performed with spiked samples and generated atmosphere [1]. All analytes are stable at least one week. All methods were validated using SKC Lot 105 coconut shell charcoal. Results were:

Compound	Methods	Range Studied mg/m³	Sample Size	Precision (s_r) Measurement	Overall
Benzyl chloride	S115 [4]	2 to 8	10 L	0.033	0.096
Bromoform	S114 [4]	3 to 10	10 L	0.047	0.071
Carbon tetrachloride	S314 [5]	65 to 299	15 L	0.037	0.092
Chlorobenzene	S133 [4]	183 to 736	10 L	0.025	0.056
Chlorobromomethane	S113 [4]	640 to 2655	5 L	0.055	0.061
Chloroform	S351 [5]	100 to 416	15 L	0.047	0.057
o-Dichlorobenzene	S135 [5]	150 to 629	3 L	0.014	0.067
p-Dichlorobenzene	S281 [5]	183 to 777	3 L	0.022	0.052
1,1-Dichloroethane	S123 [4]	212 to 838	10 L	0.011	0.057
1,2-Dichloroethylene	S110 [4]	475 to 1915	3 L	0.017	0.052
Ethylene dichloride	S122 [4]	195 to 819	3 L	0.012	0.079
Hexachloroethane	S101 [4]	5 to 25	10 L	0.014	0.121
Methyl chloroform	S328 [5]	904 to 3790	3 L	0.018	0.054
Propylene dichloride	S95 [4]	135 to 665	10 L	0.017	0.056

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] User check, UBTL, NIOSH Sequence #3990-T, S3990-U and S3990-W (unpublished, November 3, 1983).
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 1., U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[4] Ibid, V. 2., U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[5] Ibid, V. 3., U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[6] Criteria for a Recommended Standard...Occupational Exposure to Benzyl Chloride, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-182 (1978).
[7] Criteria for a Recommended Standard...Occupational Exposure to Chloroform, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 75-114 (1975).
[8] Criteria for a Recommended Standard...Occupational Exposure to Ethylene Dichloride, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-139 (1976).

[9] Criteria for a Recommended Standard...Occupational Exposure to 1,1,1-Trichloroethane, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-184 (1976).
[10] Criteria for a Recommended Standard...Occupational Exposure to Carbon Tetrachloride, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-133 (1976).

METHOD REVISED BY: G. D. Foley; Y. T. Gagnon; and K. J. Williams, NIOSH/DPSE; methods originally validated under NIOSH Contract CDC-99-74-45.

Table 1. General information.

Compounds	Formula	M.W.; mg/m³ = 1 ppm	Synonyms	OSHA NIOSH [6-10] ACGIH	BP (°C)	VP @ 20 °C	Density (g/mL @ 20 °C)
Benzyl chloride*	$C_6H_5CH_2Cl$; C_7H_7Cl	126.58; 5.17	(chloromethyl) benzene; α-chlorotoluene; CAS #100-44-7	1 ppm — 1 ppm	179	120 kPa	1.098
Bromoform	$CHBr_3$	252.75; 10.33	tribromomethane; CAS #75-25-2	0.5 ppm — 0.5 ppm (skin)	149	670 kPa	2.89
Carbon tetrachloride*	CCl_4	153.84; 6.29	tetrachloromethane; CAS #56-23-5	10 ppm, C 25 ppm 2 ppm/1 hr 5 ppm (skin), STEL 20 ppm	77	12.1 kPa	1.594
Chlorobenzene	C_6H_5Cl	112.56; 4.60	monochlorobenzene; phenyl chloride; CAS #108-90-7	75 ppm — 75 ppm	132	1.2 kPa	1.105
Chlorobromomethane	CH_2BrCl	129.39; 5.29	bromochloromethane; Halon 1011; CAS #74-97-5	200 ppm — 200 ppm, STEL 250 ppm	68	15.6 kPa	1.991
Chloroform*	$CHCl_3$	119.39; 4.88	trichloromethane; CAS #67-66-3	C 50 ppm 2 ppm/1 hr 10 ppm, STEL 50 ppm	61	21.3 kPa	1.481
o-Dichlorobenzene	$1,2\text{-}C_6H_4Cl_2$	147.00; 6.01	1,2-dichlorobenzene; CAS #95-50-1	50 ppm — C 50 ppm	180	160 kPa	1.305

Compounds	Formula	M.W.; mg/m³ = 1 ppm	Synonyms	OSHA NIOSH [6-10] ACGIH	BP (°C)	VP @ 20 °C	Density (g/mL @ 20 °C)
p-Dichlorobenzene	1,4-$C_6H_4Cl_2$	147.00; 6.01	1,4-dichlorobenzene; CAS #106-46-7	75 ppm --- 75 ppm, STEL 110 ppm	174	50 Pa	1.241
1,1-Dichloroethane	CH_3CHCl_2; $C_2H_4Cl_2$	98.96; 4.05	ethylidene chloride; CAS #75-34-3	100 ppm 100 ppm 200 ppm, STEL 250 ppm	57	24.3 kPa	1.174
1,2-Dichloroethylene	ClCH=CHCl; $C_2H_4Cl_2$	96.95; 3.96	acetylene dichloride; 1,2-dichloroethene; CAS #540-59-0	200 ppm 200 ppm 200 ppm, STEL 250 ppm	60 (cis) 47 (trans)	24-35 kPa	1.28
Ethylene dichloride*	$ClCH_2CH_2Cl$; $C_2H_4Cl_2$	98.96; 4.05	1,2-dichloroethane; CAS #107-06-2	50 ppm, C 100 ppm 5 ppm; 15 ppm/15 min 10 ppm, STEL 15 ppm	83	8.3 kPa	1.255
Hexachloroethane*	CCl_3CCl_3; C_2Cl_6	236.74; 9.68	perchloroethane; CAS #67-72-1	1 ppm (skin) 1 ppm (skin) 10 ppm	187 (sublimes)	30 Pa	2.09
Methylchloroform	CH_3CCl_3; $C_2H_3Cl_3$	133.42; 5.45	1,1,1-trichloroethane; CAS #71-55-6	350 ppm 350 ppm/15 min CAS #71-55-6 STEL 450 ppm	74 350 ppm,	13.3 kPa	1.335
Propylene dichloride	$CH_3CHClCH_2Cl$; $C_3H_6Cl_2$	112.99; 4.62	1,2-dichloropropane CAS #78-87-5	75 ppm 75 ppm 75 ppm, STEL 110 ppm	95	5.3 kPa	1.156 (25 °C)

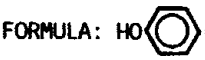
*Suspect carcinogen.

Table 2. Operational details.

Compound	Sampling: Air Sample Volume (L) Min	Sampling: Air Sample Volume (L) Max	Sampling: Breakthrough in Dry Air	Measurement: Working Range (mg/m³)	Measurement: Column*	Measurement: t (°C) Column Injector Detector	Measurement: Internal Standard	Measurement: Range (mg per sample)
Benzyl chloride	1 @ 1 ppm	10	48 L @ 8.4 mg/m³	0.5 to 15 (10 L)	A	160 170 210	n-heptadecane	0.005 to 0.15
Bromoform	1 @ 0.5 ppm	10	48 L @ 10 mg/m³	0.5 to 15 (10 L)	A	130 170 210	n-pentadecane	0.005 to 0.15
Carbon tetrachloride	2 @ 10 ppm	17	45 L @ 338 mg/m³	16 to 480 (15 L)	B	60 155 200	decane	0.2 to 7
Chlorobenzene	1 @ 75 ppm	10	44 L @ 693 mg/m³	35 to 1035 (10 L)	A	105 190 250	--	0.4 to 10
Chlorobromomethane	1 @ 200 ppm	8	8 L @ 2330 mg/m³	105 to 3150 (5 L)	A	80 170 210	n-undecane	0.5 to 15
Chloroform	1.5 @ 50 ppm	15	46 L @ 473 mg/m³	25 to 750 (15 L)	B	75 155 200	n-undecane	0.4 to 10
o-Dichlorobenzene	0.5 @ 50 ppm	3	46 L @ 655 mg/m³	30 to 900 (3 L)	C	140 225 250	nonane	0.1 to 3
p-Dichlorobenzene	1 @ 75 ppm	3	10.8 L @ 778 mg/m³	75 to 1350 (3 L)	A	140 225 275	--	0.2 to 4

Compound	Sampling: Air Sample Volume (L) Min	Max	Breakthrough in Dry Air	Measurement: Working Range (mg/m³)	Column*	t (°C) Column Injector Detector	Internal Standard	Range (mg per sample)
1,1-Dichloroethane	1 @ 100 ppm	10	18.3 L @ 838 mg/m³	40 to 1215 (10 L)	A	50 100 175	---	0.4 to 12
1,2-Dichloroethylene	0.5 @ 200 ppm	3	5.4 L @ 1909 mg/m³	80 to 2370 (3 L)	A	60 170 210	---	0.2 to 7
Ethylene dichloride	1 @ 50 ppm	10	29 L @ 821 mg/m³	40 to 1215 (3 L)	A	70 225 250	octane	0.1 to 4
Hexachloroethane	1 @ 1 ppm	10	48 L @ 23 mg/m³	1 to 30 (10 L)	D	110 170 210	n-tridecane	0.01 to 0.3
Methylchloroform	0.5 @ 350 ppm	6	9.5 L @ 3788 mg/m³	190 to 5700 (3 L)	A	70 225 250	octane	0.6 to 17
Propylene dichloride	1 @ 75 ppm	10	18 L @ 587 mg/m³	35 to 1050 (10 L)	A	80 170 210	n-undecane	0.3 to 10

*A = 3 m x 3 mm stainless steel, 10% SP-1000 on 80/100 mesh Supelcoport;
B = 6 m x 3 mm, otherwise same as A;
C = 3 m x 3 mm stainless steel, 10% OV-101 on 100/120 mesh Supelcoport; or
D = 3 m x 6 mm glass, 3% SP-2250 on 80/100 mesh Supelcoport.

FORMULA:  $C_6H_6O_2$

M.W.: 110.11

HYDROQUINONE

METHOD: 5004
ISSUED: 2/15/84

OSHA: 2 mg/m³
NIOSH: 2 mg/m³/15 min [1]
ACGIH: 2 mg/m³; STEL 4 mg/m³

PROPERTIES: solid; MP 170 °C; BP 285 °C @ 730 mm; VP 0.0024 Pa (1.8 x 10^{-5} mm Hg; 0.11 mg/m³) @ 25 °C

SYNONYMS: hydroquinol, 1,4-benzenediol, CAS #123-31-9.

SAMPLING

SAMPLER: FILTER
(0.8-µm cellulose ester membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 30 L @ 2 mg/m³
-MAX: 180 L

FIELD TREATMENT: transfer filter immediately to jar with 10 mL 1% acetic acid

SHIPMENT: ship sample solutions

SAMPLE STABILITY: at least 7 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.8 to 4 mg/m³ [2]
(90-L samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.061 [2]

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: hydroquinone

INJECTION VOLUME: 100 µL

DETECTOR: UV @ 290 nm

MOBILE PHASE: 1% acetic acid in H_2O; 1 mL/min

COLUMN: 25 cm x 4.6 mm ID Partisil 10-ODS, µ-Bondapack C_{18} or equivalent; ambient temperature, 400 to 600 psi (2800-4100 kPa)

CALIBRATION: solutions of hydroquinone in 1% aqueous acetic acid

RANGE: 0.06 to 0.8 mg per sample [3]

ESTIMATED LOD: 0.01 mg per sample [4]

PRECISION (s_r): 0.030 [2]

APPLICABILITY: The working range is 0.7 to 8 mg/m³ for a 90-L air sample or 2 to 25 mg/m³ for a 30-L air sample. This method can be used when significant concentrations of hydroquinone vapor are not present.

INTERFERENCES: None known. Hydroquinone is unstable on the collection media and must be stabilized immediately after collection by dissolution in 1% acetic acid.

OTHER METHODS: This is Method S57 [3] in a revised format. The method also appears in a NIOSH recommended standard [1].

Preceding page blank

REAGENTS:

1. Hydroquinone, reagent grade.
2. Distilled water.
3. Acetic acid, glacial.
4. Acetic acid, 1%. Dilute 10 mL acetic acid to 1 L with distilled water.
   NOTE: This solution is needed at the sampling site for field treatment of samples.
5. Calibration stock solution, 3.6 mg/mL. Dissolve 0.0900 g hydroquinone in 25 mL 1% acetic acid. Prepare fresh daily, in duplicate.

EQUIPMENT:

1. Sampler: 37-mm cassette containing 0.8-µm cellulose ester membrane filter and cellulose backup pad.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. High pressure liquid chromatograph with UV detector at 290 nm, integrator and column (page 5004-1).
4. Jars, 60-mL, ointment, low form, with PTFE film gaskets and screw caps.
5. Syringe, 100-µL, or autosampler for sample injection.
6. Microliter syringes for standard preparation.
7. Volumetic flasks, 10- and 25-mL, and 1-L.

SPECIAL PRECAUTIONS: None.

SAMPLING:

1. Calibrate each personal sampling pump with a representative filter in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 30 to 180 L.
   NOTE: This method will collect hydroquinone aerosol only. The equilibrium vapor pressure is equivalent to 0.11 mg/m^3 at 25 °C and may be a significant factor at elevated temperatures.
3. Immediately after sampling, transfer the filter (do not include backup pad) with tweezers to a 60-mL ointment jar. Add 10 mL 1% acetic acid. Process field blanks similarly.
4. Ship the filters in the ointment jars.

SAMPLE PREPARATION:

5. Transfer the sample solution from the ointment jar to a 25-mL volumetric flask.
6. Rinse the ointment jar twice with 5 mL 1% acetic acid. Add the washings to the volumetric flask. Make up to volume with 1% acetic acid.

CALIBRATION AND QUALITY CONTROL:

7. Calibrate daily with at least five working standards over the range 0.01 to 0.8 mg hydroquinone per sample.
   a. Add known amounts of calibration stock solution to 1% acetic acid in 25-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 9 and 10).
   c. Prepare calibration graph (peak area vs. mg hydroquinone).
8. Check recovery with at least three spiked media blanks per sample set.
   a. Add aliquot of calibration stock solution with a microliter syringe directly to a representative filter. Air dry.
   b. Prepare and analyze together with working standards (steps 5, 6, 9 and 10).
   c. Calculate recovery [(mg recovered - mg blank)/mg added].

MEASUREMENT:

9. Set HPLC to conditions given on page 5004-1. Inject 100-µL sample aliquot.
10. Measure peak area. Retention time is ca. 310 sec under these conditions.

CALCULATIONS:

11. Determine the mass, mg (corrected for recovery) of hydroquinone, found in the sample (W) and in the average media blank (B).
12. Calculate concentration of hydroquinone, C, in the air volume sampled, V (L):

$$C = \frac{(W - B) \cdot 10^3}{(V)}, \text{ mg/m}^3$$

EVALUATION OF METHOD:

Method S57 [3] was issued on November 26, 1976, and validated over the range 0.8 to 4 mg/m³ at 20 °C and 762 mm Hg using 90-L air samples [2,5]. Overall precision, s_r, was 0.061 with average recovery 105%, representing a non-significant bias. The atmospheres were generated by atomization of an aqueous solution of hydroquinone into dry air; aerosol concentrations were independently verified by direct UV spectrophotometry on filter samples. Average collection efficiency was 100% at 4 mg/m³. No loss of hydroquinone was seen from filters spiked with 720 µg hydroquinone, and then used to sample 180 L clean air, indicating the hydroquinone vapor pressure is not significant at these conditions. At elevated temperature, however, contribution from vapor may be significant. Storage studies were conducted by storing exposed filters in 1% acetic acid at ambient temperature for seven days. No change in hydroquinone concentration was seen.

REFERENCES:

[1] Criteria For A Recommended Standard-Occupational Exposure to Hydroquinone, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-155 (1978).
[2] Backup Data Report No. S57, NIOSH Contract 210-76-0123 (unpublished, 1976), available as "Ten NIOSH Analytical Methods, Set 2," Order No. PB 271-464, from NTIS, Springfield, VA 22161.
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 2, S57, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[4] User check, A. D. Little, Inc., NIOSH Sequence #4121Q (unpublished, October 25, 1983).
[5] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY: Jerome Smith, Ph.D., NIOSH/DPSE; S57 originally validated under NIOSH Contract 210-76-0123.

FORMULA: RNCO

ISOCYANATE GROUP

METHOD: 5505
ISSUED: 2/15/84

M.W.: varies

OSHA: C 20 ppb (MDI and TDI)
NIOSH: 5 ppb/10 hr; 20 ppb/10 min (diisocyanates) [1]
ACGIH: C 20 ppb (MDI); 5 ppm (TDI)

PROPERTIES: depend on R- to which isocyanate group is attached; R- may be aromatic, aliphatic, monomeric or polymeric

SYNONYMS: various [1], including 4,4'-methylenediphenyl isocyanate (MDI; CAS #101-68-8); 2,4-toluene diisocyanate (TDI; CAS #584-84-9).

SAMPLING

SAMPLER: IMPINGER (solution of 1-(2-methoxyphenyl)-piperazine in toluene)

FLOW RATE: 1 L/min

VOL-MIN: 350 L
-MAX: 600 L

SHIPMENT: in vials; flammable liquid

SAMPLE STABILITY: $\geq$ 2 weeks

BLANKS: 2 to 10 field blanks per set + 1 initial reagent blank

ACCURACY

RANGE STUDIED: not studied

BIAS: not determined

OVERALL PRECISION (s_r): not evaluated

MEASUREMENT

!TECHNIQUE: HPLC, UV DETECTION
!
!ANALYTE: 1-(2-methoxyphenyl)piperazine
!
!PREPARATION: acetylate analyte; evaporate toluene; dissolve residue in methanol
!
!INJECTION VOLUME: 10 µL
!
!MOBILE PHASE: 50/50 acetonitrile/0.015 M sodium acetate; pH 6; 1.5 mL/min
!
!COLUMN: octylsilylated silica (C_8), 10-µm particle size, 25 cm x 4.2 mm
!
!DETECTOR WAVELENGTH: 254 nm
!
!CALIBRATION: solutions of 1-(2-methoxyphenyl)-piperazine in methanol
!
!RANGE: 0.24 to 3.5 µmol NCO group per sample
!
!ESTIMATED LOD: 0.2 µmol NCO group per sample
!
!PRECISION (s_r): 0.048 [2]

APPLICABILITY: This method is used to determine the total concentration of the isocyanate group, regardless of the molecule to which the isocyanate group is attached. Monomeric isocyanates can be individually determined with this sampling reagent [3]. Concentrations of ureas from monomeric isocyanates and 1-(2-methoxyphenyl)piperazine can be determined simultaneously. NIOSH has used this method to sample for isocyanate groups and monomeric 2,4-toluene diisocyanate in a urethane foam manufacturing plant.

INTERFERENCES: Phosgene, acid halides and possibly some esters will react with 1-(2-methoxyphenyl)piperazine, consume reagent, and cause a positive bias.

OTHER METHODS: P&CAM 141, 142, 326, and 347 [4,5,6] are for monomeric species only and which are subject to amine interference or use an unstable derivatizing agent. Recent reviews have been published [7,8].

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REAGENTS:

1. Sampling medium:* 1-(2-methoxyphenyl)piperazine in toluene (see APPENDIX).
   NOTE: Reserve 10 mL of this solution for analysis (step 15).
2. Acetic anhydride.
3. Methanol.*
4. Acetonitrile.
5. Deionized water.
6. Pentane.
7. Sodium acetate, anhydrous.
8. Acetic acid, glacial.
9. Nitrogen.
10. Toluene.*
11. Calibration stock stolution, 1 µg/µL. Dissolve 1-(2-methoxyphenyl)piperazine in methanol.
12. Mobile phase. Dissolve 1.2 g sodium acetate in 1 L deionized water. Add 1 L acetonitrile. Add glacial acetic acid as needed to bring the pH to 6.0.

*See Special Precautions.

EQUIPMENT:

1. Sampler: midget impinger, 25-mL.
2. Personal sampling pump, 1 L/min, with flexible connecting tubing.
3. Glass-marking pen.
4. Liquid chromatograph with a UV detector, recorder, integrator and column (page 5505-1).
5. Ultrasonic waterbath.
6. Vials, 20-mL glass, with polypropylene-lined screw caps.
7. Vials, 4-mL glass, with screw caps.
8. Pasteur pipets, 7-cm glass, disposable.
9. Volumetric flasks, 10-mL.
10. Syringes, sizes appropriate for preparing standard solutions.
11. Pipets, 2- and 15-mL glass, delivery, with pipet bulb.
12. Hotplate.
13. Beakers, 250-mL.
14. Evaporator, Mini-Vap, 6 port, or equivalent.
15. Flask, filtration, 500-mL.
16. Funnel, Buchner, fritted glass, medium porosity, 100-mL.
17. Vacuum pump.
18. Flask, 50-mL, round bottom.
19. T-adapter, with stopcock.
20. pH meter.

SPECIAL PRECAUTIONS: Sample and standard preparation should be done in hood to avoid exposure to toluene and methanol vapors.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Transfer 15.0 mL sampling medium to an impinger. Mark the solution level on the impinger with a glass-marking pen.
3. Connect the assembled impinger to a sampling pump. If it is necessary to add solvent during sampling for proper impinger operation, add only toluene. Do not add more sampling medium.
   NOTE: If an area sample is being taken, the impinger may be packed in ice during sampling to retard toluene losses.
4. Sample 350 to 600 L of air at a sampling rate of 1 L/min.
5. Bring sample solution level back to the pre-sampling mark (15.0 mL) by adding toluene.
6. Transfer the sample solution to a 20-mL vial for shipment. Do not rinse the impinger.

SAMPLE PREPARATION:

7. Transfer a 2-mL aliquot to a 4-mL vial for evaporating.
8. Add 10 µL acetic anhydride to acetylate the 1-(2-methoxyphenyl)piperazine.
9. Evaporate toluene from sample under a stream of nitrogen while warming the sample on a 40 to 50 °C hotplate.

10. Add 200 µL methanol after sample has reached complete dryness.
11. Agitate sample in an ultrasonic bath for 15 min to dissolve residue.

CALIBRATION AND QUALITY CONTROL:

12. Prepare working standards (25 to 450 µg/mL) by adding appropriate aliquots of calibration stock solution to 2 to 3 mL methanol in a 10-mL volumetric flask. Add 10 µL acetic anhydride. Mix and dilute to the mark with methanol.
13. Analyze working standards together with samples and blanks (steps 16 through 18). Prepare a calibration graph of area vs. amount (µg) of 1-(2-methoxyphenyl)piperazine per 15 mL original solution.
    NOTE: The amount present in an original 15-mL sample is 1.5 times the concentration of the analyzed solution: (0.2 mL/aliquot) • (7.5 aliquots/sample).
14. Prepare control samples by adding a known amount of a monomeric isocyanate to 15.0 mL sampling medium and performing steps 7-11 and 16-19.
15. Analyze three 2-mL aliquots of the sampling medium from the same batch used for sampling (Reagent 1.).
    NOTE: These are not the same as field blanks.

MEASUREMENT:

16. Set up the HPLC system according to manufacturer's recommendations and to the conditions given on page 5505-1.
17. Inject a 10-µL concentrated sample aliquot.
18. Measure peak area.

CALCULATIONS:

19. Read amount, M_S (µg), of 1-(2-methoxyphenyl)piperazine per 15 mL sample from calibration graph for each sample.
20. Calculate the initial amount of reagent, µg, present before sampling, M_I, by averaging the amount determined for the three samples prepared from sampling medium not taken into the field (step 15).
21. Calculate the concentration of isocyanate groups, C (µmol/m³), in the air volume sampled, V (L):

$$C = \frac{(M_I - M_S) \cdot 10^3}{(192.26) \cdot (V)}, \ \mu mol/m^3.$$

where 192.26 is the molecular weight of 1-(2-methoxyphenol)piperazine.

EVALUATION OF METHOD:

Lab-tested with 2,4-toluene diisocyanate spiked samplers with independent quantitation of isocyanate groups from measurement of isocyanate urea [2]. The average recovery for the sample preparation procedure of 1-(2-methoxyphenyl)piperazine, as the acetyl derivative, was determined to be 96% over a range of 8.2 to 813 µg per 15-mL sample. Toluene solutions of 1-(2-methyoxyphenyl)piperazine (15.7 µg per 15-mL sample) were stored at room temperature for two weeks with no loss of 1-(2-methoxyphenyl)piperazine. Precision was determined from the analysis of 21 samples which were prepared by adding known quantities of monomeric 2,4-toluene diisocyanate (0.24 to 3.2 µmole) to 1-(2-methoxyphenyl)piperazine in toluene (43 µg/mL).

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Diisocyanates, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-125 (1978).

[2] Seymour, M. J. "Determination of Isocyanate Group Concentrations in Air by Derivatization with 1-(2-Methoxyphenyl)piperazine and Analysis by High Performance Liquid Chromatography" (in preparation).
[3] Warwick, C. J., D. J. Bagon and C. V. Purnell, Analyst, 106, 676-685 (1981).
[4] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 141 and 142, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[5] Ibid, V. 6, P&CAM 326, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).
[6] Ibid, V. 7, P&CAM 347, U.S. Department of Health and Human Services, Publ. (NIOSH) 82-100 (1982).
[7] Melcher, R. G., Anal. Chem. 55, 40R-56R (1983).
[8] Purnell, C. J. and R. F. Walker, Anal. Proc. 18, 472-478 (1981).

APPENDIX:

PURIFICATION OF 1-(2-METHOXYPHENYL)PIPERAZINE AND PREPARATION OF SAMPLING MEDIUM:
Place 25 g 1-(2-methoxyphenyl)piperazine (yellowish white solid) in a 250-mL beaker. Add approximately 125 mL pentane. Bring to a boil on a hotplate and allow to boil until all but a small amount of yellow oil is in solution. The 1-(2-methoypheny1)piperazine will melt as it is warmed in the pentane. Decant the solution into a clean beaker, cover with a watchglass and then cool in the freezer for 2 to 3 hrs. White fluffy crystals will form. Filter with a Buchner funnel. Transfer the crystals to a 50-mL round bottom flask and dry briefly under vacuum to remove final traces of pentane. Store the hygroscopic crystals in an air-tight container in a refrigerator. The melting range of the crystals is 26-29 °C.

Prepare the sampling medium using the purified 1-(2-methoxyphenyl)piperazine. Dissolve this reagent in toluene at a concentration of 43 µg/mL.

METHOD WRITTEN BY: Martha Seymour and A. W. Teass, Ph.D., NIOSH/DPSE.

FORMULA: $(CH_3)_2$ CH_3; $C_9H_{14}O$

M.W.: 138.21

ISOPHORONE

METHOD: 2508
ISSUED: 2/15/84

OSHA: 25 ppm
NIOSH: 4 ppm [1]
ACGIH: C 5 ppm
(1 ppm = 5.65 mg/m³ @ NTP)

PROPERTIES: liquid; d 0.923 g/mL @ 25 °C;
BP 213 °C; MP -80 °C;
VP 26 Pa (0.2 mm Hg; 260 ppm) @ 20 °C;
explosive range 0.8 to 3.8% v/v in air

SYNONYMS: 3,5,5-trimethyl-2-cyclohexen-1-one; CAS #78-59-1.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(petroleum-based charcoal,
100 mg/50 mg)

FLOW RATE: 0.01 to 1 L/min

VOL-MIN: 2 L
-MAX: 25 L

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 67 to 283 mg/m³ [2]

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.058 [2]

MEASUREMENT

!
!TECHNIQUE: GAS CHROMATOGRAPHY, FID
!
!ANALYTE: isophorone
!
!DESORPTION: 1 mL CS_2; stand 30 min
!
!INJECTION VOLUME: 5 µL
!
!TEMPERATURE-INJECTOR: 200 °C
! -DETECTOR: 250 °C
! -COLUMN: 160 °C
!
!CARRIER GAS: N_2 or He, 30 mL/min
!
!COLUMN: 4 m x 3 mm glass, 10% SP2100/0.1%
! Carbowax 1500 on 100/120 Supelcoport
! or equivalent
!
!CALIBRATION: isophorone in CS_2
!
!RANGE: 0.2 to 10 mg per sample [3]
!
!ESTIMATED LOD: 0.02 mg per sample
!
!PRECISION (s_r): 0.033 [2,3]
!

APPLICABILITY: The working range for this method is 2 to 400 mg/m³ for a 12-L air sample. High humidity will greatly decrease breakthrough volume.

INTERFERENCES: None identified. Alternate columns may be used, e.g., 10% SP-1000 or DB-2 fused silica capillary column.

OTHER METHODS: This is Method S367 with a different column recommended [3].

REAGENTS:
1. Carbon disulfide, chromatographic grade.*
2. Isophorone.*
3. Nitrogen, prepurified.
4. Hydrogen, prepurified.
5. Air, filtered.

*See Special Precautions.

EQUIPMENT:
1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing two sections of 20/40 mesh petroleum-based charcoal (100 mg front/50 mg back) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 2508-1).
4. Vials, 2-mL, PTFE-lined caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Volumetric flasks, 10-mL.
7. Pipet, 1-mL, with pipet bulb.

SPECIAL PRECAUTIONS: CS_2 is toxic and acute fire and explosion hazard (flash point = -30 °C); work with it only in a hood.

Isophorone is a lachrymator [1]; work with it should be done in a hood and caution should be taken while it is being used.

SAMPLING:
1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 1 L/min for a total sample size of 2 to 25 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:
5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL CS_2 to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:
8. Calibrate daily with at least five working standards over the range 0.02 to 10 mg isophorone per sample.
   a. Add known amounts of isophorone to CS_2 in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg isophorone).

9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of isophorone directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg isophorone recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2508-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with CS_2, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of isophorone found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of isophorone in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

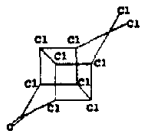
EVALUATION OF METHOD:

Method S367 [3] was validated over the range 69 to 304 mg/m³ using a 12-L sample [2]. Overall precision, s_r, was 0.059 with an average recovery of 104.9%, representing a non-significant bias. The concentration was independently verified by a direct hydrocarbon analyzer. Desorption efficiency was 0.860 in the range of 0.849 to 3.40 mg per sample. No breakthrough occurred when an atmosphere containing 283 mg/m³ was sampled for 240 min at a rate of 0.19 L/min. At this time the breakthrough test was discontinued. Samples are stable for at least one week at room temperature.

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Ketones, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-173 (1978).
[2] Documentation of the NIOSH Validation Tests, S367-1 to S367-6, U.S. Department of Health and Human Services, Publ. (NIOSH) 77-185 (1977).
[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3, S367, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

METHOD REVISED BY: Edward Slick, NIOSH/DPSE; S367 originally validated under NIOSH Contract CDC-99-74-45.

FORMULA:  $;C_{10}Cl_{10}O$

M.W.: 490.68

KEPONE

METHOD: 5508
ISSUED: 2/15/84

OSHA: no standard
NIOSH: 0.001 mg/m³ [1]
ACGIH: no standard

PROPERTIES: solid; MP 349 °C;
VP <4 x 10^{-5} Pa (3 x 10^{-7} mm Hg;
8 µg/m³) @ 25 °C

SYNONYMS: chlordecone; CAS #143-50-0.

SAMPLING

SAMPLER: FILTER + IMPINGER
(0.8-µm cellulose ester membrane
+ impinger with 0.1 M NaOH)

FLOW RATE: 1 L/min

VOL-MIN: 80 L @ 1 µg/m³
-MAX: 600 L

SHIPMENT: routine

SAMPLE STABILITY: at least 12 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 2.5 to 2.6 µg/m³
(376-L samples)

BIAS: not determined

OVERALL PRECISION (s_r): 0.23

MEASUREMENT

!
!TECHNIQUE: GAS CHROMATOGRAPHY, ECD
!
!ANALYTE: Kepone
!
!RECOVERY FROM FILTER: 99:1 benzene:methanol,
! 10 mL; stand 2 hrs
!
!RECOVERY FROM IMPINGER: extract @ pH <7 with two
! 5-mL portions of benzene
!
!INJECTION VOLUME: 5 µL
!
!TEMPERATURE-INJECTION: 225 °C
! -DETECTOR: 335 °C
! -COLUMN: 200 °C
!
!CARRIER GAS: nitrogen, 70 mL/min
!
!COLUMN: 1.8 m x 4 mm glass; 3% OV-1 on 80/100
! mesh Chromosorb W HP
!
!CALIBRATION: Kepone in 99:1 benzene:methanol
!
!RANGE: 50 to 500 ng per sample
!
!ESTIMATED LOD: 10 ng per sample
!
!PRECISION (s_r): 0.014 (filters);
! 0.060 (impingers)
!

APPLICABILITY: The working range is 0.001 to 10 mg/m³ for 80-L air samples. Personal and area samples were collected by this method at a Mirex formulation plant.

INTERFERENCES: Partial conversion of Mirex into Kepone can occur by reaction with NaOH solution in the impinger and pH adjustment. A different column packing which may be used is 3% OV-210 on 80/100 mesh Chromosorb W HP.

OTHER METHODS: This method was originally designated P&CAM 225 [2].

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REAGENTS:

1. Sodium hydroxide, 0.1 M, aqueous.
2. Benzene, pesticide quality.*
3. Methanol, pesticide quality.*
4. Benzene:methanol, 99:1 (v/v).*
5. Sulfuric acid, 0.05 M.
6. Kepone.*
7. Calibration stock solution, 50 µg/mL. Dissolve 100 mg Kepone in 99:1 benzene:methanol to make 10 mL solution. Dilute 50 µL of this solution to 10 mL with 99:1 benzene:methanol. Stable at least one week at 25 °C.
8. Impinger recovery stock solution, 1 µg/mL. Dissolve 25 mg Kepone in methanol to make 10 mL solution. Dilute 4 µL of this solution to 10 mL with methanol.

*See Special Precautions.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-µm, 37-mm, in a filter holder followed by a midget impinger with 15 mL 0.1 M NaOH. (Filter holder and impinger connected with a 2-cm piece of plastic tubing.)
2. Sampling pump, 1 L/min, with flexible connecting tubing.
3. Impinger, midget, with stem removed.
4. Gas chromatograph, electron-capture detector, integrator and column (page 5508-1).
5. Forceps, two pairs.
6. Volumetric flasks, 10-mL.
7. Separatory funnel, 125-mL.
8. Syringes, 10-µL, readable to 0.1-µL; 100-µL, readable to 1 µL.
9. pH paper.
10. Pipet, 5-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Methanol and benzene are flammable.

Benzene and Kepone [1] are carcinogens.

SAMPLING:

1. Connect the outlet of the impinger containing 15 mL 0.1 M NaOH and the inlet of the sampling pump to an empty impinger without a stem to protect the sampling pump from splash over.
2. Calibrate the sampling pump with a representative sampler in line.
3. Sample at 1 L/min for 1.3 to 10 hrs (80 to 600 L). Do not exceed 2 mg total dust loading on the filter.
4. Separate the filter cassette and impinger for shipment to the laboratory.

SAMPLE PREPARATION:

5. Use forceps to fold and transfer the filter to a 10-mL volumetric flask.
6. Add 10.0 mL 99:1 benzene:methanol.
7. Stopper and shake the flask vigorously for 1 min. Allow the flask to stand at least 2 hrs.
8. Transfer the solution in the impinger to a separatory funnel. Wash the impinger with two 15-mL portions of 0.1 M NaOH, and add the washings to the separatory funnel. Add 0.05 M H_2SO_4 until the pH is less than 7.
9. Extract the Kepone with two 5-mL portions of benzene. Shake vigorously for 2 min and allow 5 min for the phases to separate. Combine the benzene layers in a 10-mL volumetric flask. Add 100 µL methanol and benzene to the mark.

CALIBRATION AND QUALITY CONTROL:

10. Prepare a series of working standards in the range 1 to 50 ng/mL by diluting 50 µg/mL calibration stock solution with 99:1 benzene:methanol to 3.6 µg/mL and diluting this solution.

11. Analyze the working standards according to steps 15 through 17.
12. Prepare a calibration graph of peak area or peak height vs. mass of Kepone in ng per sample.
13. Determine the average recovery of Kepone from filters.
    a. Fortify six filters with about 7 µL of 50-µg/mL calibration stock solution.
    b. Allow the filters to air dry.
    c. Prepare samples according to steps 5 through 7.
    d. Analyze samples with standards according to steps 15 through 17.
    e. Calculate the average recovery, R (mass of Kepone found divided by mass of Kepone applied).
14. Determine the average recovery of Kepone from impingers.
    a. Fortify each of six impingers containing 15 mL 0.1 M NaOH solution with 100 µL 1-µg/mL impinger recovery stock solution.
    b. Prepare samples according to steps 8 and 9.
    c. Analyze samples with standards according to steps 15 through 17.
    d. Calculate the average recovery.

MEASUREMENT:

15. Set the gas chromatograph to conditions given on page 5508-1. t_r of Kepone = 4.6 min, and t_r of Mirex = 9.2 min for these conditions.
16. Inject 5-µL aliquots of sample solutions and standards using solvent-flush technique.
    NOTE: Rinse the syringe thoroughly after each injection with methanol and then with benzene; otherwise traces of Kepone will remain in the syringe.
17. Measure peak area or peak height.

CALCULATIONS:

18. Determine the quantities in ng of Kepone on the filter (W_f), in the impinger (W_i), in the average filter blank (B_f), and in the average impinger blank (B_i) from calibration graphs based on standards analyzed with the samples.
19. Calculate the concentration, C (µg/m³), of Kepone in the air volume sampled, V (L):

$$C = \frac{W_f - B_f}{RV} + \frac{W_i - B_i}{V}, \ \mu g/m^3.$$

EVALUATION OF METHOD:

This method was tested with fortified filters, fortified NaOH solutions and controlled atmospheres near 25 °C. The relative standard deviation (s_r) for filters was 0.23 (10 samples, pooled) for 376-L samples at 2.5 and 2.6 µg/m³. Quantities of Kepone found in impingers were less than 50 ng. The quantity of Kepone found in each impinger corresponded to about 0.1 ng or less for each liter of air in a sample. Collection efficiencies of impingers were roughly 50%. Average recovery of 360 ng of Kepone from filters was 0.89; s_r was 0.014 for six samples. Kepone was stable on filters at room temperature for 12 days. Average recovery of 45 ng Kepone from 45-mL aliquots of 0.1 M NaOH solution was 1.01; s_r was 0.060 for 8 samples. Average recovery of 79 ng Kepone from 10-mL aliquots of 0.1 M NaOH solution was 1.13 after 14 days of storage at room temperature. Personal and area samples (45 to 84 L) were collected by this method at a Mirex formulation plant. Mirex was found on filters in quantities of 240 to 1240 µg and in impingers in quantities of 0.3 to 16 µg. Although no Kepone was detected on filters, Kepone in quantities of 0.1 to 2 µg was found in impingers. Most or all of the Kepone in each impinger was produced by chemical conversion of Mirex.

REFERENCES:
[1] NIOSH Recommended Standard for Occupational Exposure to Kepone, U.S. Department of Health, Education, and Welfare, (NIOSH), unnumbered publication (January, 1976).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 225, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).

METHOD WRITTEN BY: Samuel P. Tucker, Ph.D., James J. Sweeney, John McFeters, and Alexander W. Teass, Ph.D., NIOSH/DPSE.

FORMULA: Table 1

M.W.: Table 1

KETONES I

METHOD: 1300
ISSUED: 2/15/84

OSHA/NIOSH/ACGIH: Table 1

PROPERTIES: Table 1

COMPOUNDS: (Synonyms in Table 1)	acetone	methyl isobutyl ketone	2-hexanone
	cyclohexanone	2-pentanone	diisobutyl ketone

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

	acetone	others
VOL-MIN:	0.5 L	1 L
-MAX:	3 L	25 L

SHIPMENT: normal

SAMPLE STABILITY: unknown

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED, BIAS and OVERALL PRECISION (s_r): see EVALUATION OF METHOD

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 1 mL CS_2, stand 30 min

INJECTION VOLUME: 5 µL

COLUMN: glass (12 ft x 1/4 inch); 10% SP-2100
0.1% Carbowax 1500 on Supelcoport
100/120

TEMPERATURE-INJECTOR: 250 °C
-DETECTOR: 300 °C
-COLUMN: 50 °C to 170 °C @ 10°/min

CARRIER GAS: N_2 or He, 30 mL/min

CALIBRATION: standard solutions of analyte in CS_2

RANGE: see EVALUATION OF METHOD

ESTIMATED LOD: 0.02 mg per sample

PRECISION (s_r): see EVALUATION OF METHOD

APPLICABILITY: This method is intended as a general method for the ketones listed above. If only certain compounds are of interest, the instrumental conditions can be changed to maximize instrument response for these compounds.

INTERFERENCES: None reported. Alternate columns, e.g., 10% SP-2100 or DB-1 fused silica capillary, can be used.

OTHER METHODS: This method combines and replaces Methods S1, S18, S19 and S20 [1] and S178 and S358 [2].

REAGENTS:
1. Carbon disulfide (GC grade).*
2. Analytes, reagent grade.
3. Nitrogen, prepurified.
4. Hydrogen, dry.
5. Air, filtered, dry.

*See Special Precautions.

EQUIPMENT:
1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph equipped with FID, integrator and column (page 1300-1).
4. Vials, 2-mL, glass, PTFE-lined crimp caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Pipets, various sizes for preparing standards, with pipet bulb.
7. Volumetric flasks, 5- and 10-mL, for standards.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); work with it only in a hood.

SAMPLING:
1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 0.5 to 3 L for acetone or 1 to 25 L for the other analytes.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:
5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL CS_2 to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:
8. Calibrate daily with at least five working standards over the range 0.02 to 10 mg analyte per sample.
   a. Add known amounts of analyte to CS_2 in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of analyte directly onto front sorbent section with a microliter syringe.

c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg analyte recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1300-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with CS_2, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

The methods were validated under NIOSH Contract CDC-99-74-45 [3]. Desorption efficiency was checked by spiking known amounts of the compounds (either neat or in solutions with CS_2) on coconut shell charcoal. Samples were generated for acetone, cyclohexanone, 2-pentanone, and methyl isobutyl ketone by heating a quantity of the liquid to just below its boiling point in a 3-necked, 500-mL round bottom flask. The compound was carried through a fixed-temperature condenser to the concentrations. Samples were generated for diisobutyl ketone and 2-hexanone using a syringe pump which delivered the compounds to a heated glass-lined inlet which was swept with nitrogen, carrying the vapor to the mixing chamber. Results were as follows:

Compound	Method [1,2]	Overall			Measurement		
		Range (mg/m^3)	Breakthrough[1] (L)	S_r	Range (mg per sample)	DE[2]	S_r
Acetone	S1 [1,3]	1200 to 4500	4.3	0.082	2.4 to 14.2	0.86	0.024
Cyclohexanone	S19 [1,3]	98 to 392	65	0.062	3.8 to 18.0	0.82	0.025
Hexanone	S18 [1,3]	208 to 836	17	0.064	2.1 to 8.3	0.91	0.008
2-Pentanone	S20 [1,3]	395 to 1570	19	0.063	3.5 to 14.0	0.90	0.011
2-Hexanone	S178 [2,3]	188 to 790	>45	0.053	1.5 to 8.1	0.81	0.018
Diisobutyl ketone	S358 [2,3]	145 to 582	44	0.070	1.8 to 7.0	0.97	0.032

[1]5% breakthrough, 0.2 L/min at high end of concentration range in dry air.
[2]Averaged over mass range shown.

REFERENCES:
[1] NIOSH Manual of Analytical Methods, 2nd. ed., V. 2, S1, S18, S19 and S20, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[2] Ibid, V. 3, S178 and S358, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[3] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).

METHOD REVISED BY: Edward J. Slick, NIOSH/DPSE; methods originally validated under NIOSH Contract CDC-99-74-45.

Table 1. General information.

Compound (Synonyms)	Formula (M.W.)	Exposure Limits, ppm OSHA	NIOSH	ACGIH TLV STEL	mg/m³/ppm @ NTP	Properties*
Acetone (2-Propanone; CAS #67-64-1)	CH_3COCH_3; C_3H_6O (58.08)	1000	250	750 1000	2.37	liquid; BP 56 °C; d 0.791 g/mL; VP 35.5 kPa (266 mm Hg)
Cyclohexanone (CAS #108-94-1)	=O; $C_6H_{10}O$ (98.15)	50	25	25 100	4.01	liquid; BP 155 °C; d 0.947 g/mL; VP 0.3 kPa (2 mm Hg)
Methyl isobutyl ketone (MIBK; hexone; 4-methyl-2-pentanone; CAS #108-10-1)	$(CH_3)_2CHCH_2COCH_3$; $C_6H_{12}O$ (100.16)	100	50	50 75 (skin)	4.09	liquid; BP 117 °C; d 0.800 g/mL; VP 2.0 kPa (15 mm Hg)
2-Pentanone (methyl propyl ketone; CAS #107-87-9)	$CH_3CH_2CH_2COCH_3$; $C_5H_{10}O$ (86.13)	200	150	200 250	3.52	liquid; BP 100 °C; d 0.812 g/mL, VP 3.6 kPa (27 mm Hg)
2-Hexanone (methyl n-butyl ketone; MBK; CAS #591-78-6)	$CH_3(CH_2)_3COCH_3$; $C_6H_{12}O$ (100.16)	100	1	5 --	4.09	liquid; BP 127 °C; d 0.812 g/mL; VP 0.4 kPa (3 mm Hg)
Diisobutyl ketone (2,6,-dimethyl-4-heptanone; CAS #108-83-8)	$((CH_3)_2CHCH_2)_2CO$; $C_9H_{18}O$ (142.24)	50	25	25 --	5.82	liquid; BP 169 °C; d 0.847 g/mL; VP 0.23 kPa (1.7 mm Hg)

*Density @ 25 °C; VP @ 20 °C.

FORMULA: Table 1

M.W.: Table 1

KETONES II

METHOD: 1301
ISSUED: 2/15/84

OSHA/NIOSH/ACGIH: Table 1

PROPERTIES: Table 1

COMPOUNDS: (Synonyms in Table 1)
camphor
mesityl oxide
5-methyl-3-heptanone
methyl-(n-amyl)-ketone
ethyl butyl ketone

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L
-MAX: 25 L

SHIPMENT: normal

SAMPLE STABILITY: unknown

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED, BIAS and
OVERALL PRECISION (s_r): see EVALUATION OF METHOD

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPH, FID

ANALYTE: compounds above

DESORPTION: 1 mL 1% methanol in CS_2; stand 30 min

INJECTION VOLUME: 5 µL

COLUMN: stainless steel (3 m x 3 mm ID), 10% FFAP on 80/100 Chromosorb W-AW

TEMPERATURE-INJECTOR: 200 °C
-DETECTOR: 300 °C
-COLUMN: 100 to 200 °C @ 10 °C/min

CARRIER GAS: N_2 or He, 30 mL/min

CALIBRATION: standard solutions of analyte in elution solvent

RANGE and PRECISION: see EVALUATION OF METHOD

ESTIMATED LOD: 0.05 mg per sample

APPLICABILITY: This method was developed to give better desorption than obtainable with carbon disulfide extraction of the charcoal. This method can be used in paint and resin manufacturing plants.

INTERFERENCES: None reported. Alternate columns, e.g., 4 m 10% SP-2100/0.1% Carbowax 1500 on Supelcoport 100/120 or DB-1 fused silica capillary may be used.

OTHER METHODS: This method combines and replaces Methods S10, S12, S13, S15 and S16 [1].

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REAGENTS:

1. Eluent: Carbon disulfide* (chromatographic grade) with 1% (v/v) methanol (chromatographic grade).
2. Analytes, reagent grade.
3. Nitrogen, prepurified.
4. Hydrogen, dry.
5. Air, filtered.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing two sections of 20/40 mesh activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg), separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube must be less than 3.4 kPa at the sampling flow rate. Tubes are commercially available.
2. Personal sampling pump, 0.02 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1301-1).
4. Vial, 2-mL glass, PTFE-lined crimp caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Pipet, 1-mL, with pipet bulb.
7. Volumetric flasks, 10 mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); all work done with it must be performed in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 1 to 25 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.01 to 0.5 mg camphor; and 0.05 to 5 mg of the other analytes per sample.
   a. Add known amounts of analyte to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of analyte directly onto front sorbent section with a microliter syringe.

c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg analyte recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1301-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Laboratory testing with spiked samples and atmosphere generated by syringe pump/air dilution; verified by FID continuous monitor [2]. Results were:

Compound	Method [1,2]	Overall Range (mg/m³)	Overall Breakthrough[1] (L)	Overall s_r	Measurement Range (mg per sample)	Measurement DE[2]	Measurement s_r
Camphor	S10	6 to 25	>48	0.074	0.02 to 0.40	0.97	0.018
Mesityl oxide	S12	45 to 210	>48	0.071	0.10 to 3.0	0.81	0.014
5-Methyl-3-heptanone	S13	60 to 270	>36	0.10	0.15 to 4.0	0.90	0.014
Methyl-(n-amyl)-ketone	S15	200 to 925	>36	0.066	0.5 to 10.0	0.82	0.012
Ethyl butyl ketone	S16	100 to 460	>24	0.086	0.25 to 7.0	0.94	0.022

[1]5% breakthrough, 0.2 L/min, at high end of concentration range in dry air.
[2]Averaged over mass range shown.

REFERENCES:
[1] NIOSH Manual of Analytical Methods, 2nd. ed., V. 2, S10, S12, S13, S15, S16, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[2] Documentation of the NIOSH Validation Tests, S10, S12, S13, S15, S16, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).

METHOD REVISED BY: Edward Slick, NIOSH/DPSE; methods originally validated under NIOSH Contract CDC-99-74-45.

Table 1. General information.

Compound (Synonyms)	Formula (M.W.)	Exposure Limits, ppm OSHA	NIOSH	ACGIH TLV STEL	mg/m³/ppm @ NTP	Properties*
Camphor (CAS #76-22-2)	$C_{10}H_{16}O$ (152.24)	2	2	2 3	6.22	solid; d 0.992 g/mL @ 25 °C; MP 174 °C; VP 0.024 kPa (0.18 mm Hg; 1470 mg/m³); sublimes
Mesityl oxide (4-methyl-3-penten-2-one) (CAS #141-79-7)	$CH_3COCH=C(CH_3)_2$; $C_6H_{10}O$ (98.15)	25	10	25 ---	4.01	liquid; BP 129 °C; VP 1.1 kPa (8 mm Hg); d 0.822 g/mL
5-Methyl-3-heptanone (Ethyl amyl ketone) (CAS #106-68-3)	$CH_3CH_2COCH_2\underset{CH}{\underset{\diagdown}{\diagup}}CHCH_2CH_3$; $C_8H_{16}O$ (122.22)	25	25	25 ---	5.00	liquid; BP 159 °C; VP 0.27 kPa (2 mm Hg); d 0.822 g/mL
Methyl-(n-amyl)-ketone (2-Heptanone) (CAS #110-43-0)	$CH_3CO(CH_2)_4CH_3$; $C_7H_{14}O$ (114.19)	100	100	100 150	4.67	liquid; BP 151 °C; VP 0.27 kPa (2 mm Hg); d 0.820 g/mL
Ethyl butyl ketone (3-heptanone) (CAS #106-35-4)	$CH_3CH_2CO(CH_2)_3CH_3$; $C_7H_{14}O$ (114.19)	50	50	50 75	4.67	liquid; BP 148 °C; VP 0.53 kPa (4 mm Hg); d 0.818 g/mL

*NOTE: All densities and vapor pressures are at 20 °C unless stated otherwise.

FORMULA: Pb

M.W.: 207.19 (Pb); 223.19 (PbO)

LEAD

METHOD: 7082
ISSUED: 2/15/84

OSHA: 0.05 mg/m³
NIOSH: 0.05 mg/m³ [1]
ACGIH: 0.15 mg/m³; STEL 0.45 mg/m³

PROPERTIES: soft metal;
d 11.3 g/cm³; MP 327.5 °C;
valences +2, +4 in salts

SYNONYMS: vary depending upon the chemical form (elemental lead and lead compounds except alkyl lead); CAS #1317-36-8 (PbO); CAS #7439-92-1 (Pb).

SAMPLING

SAMPLER: FILTER
(0.8-µm cellulose ester membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 200 L @ 0.05 mg/m³
-MAX: 1200 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.13 to 0.4 mg/m³ [2];
0.15 to 1.7 mg/m³ (fume) [3]

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.072 [2];
0.068 (fume) [3]

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, FLAME

ANALYTE: lead

ASHING: conc. HNO_3, 6 mL; 140 °C

FINAL SOLUTION: 10% HNO_3, 10 mL

FLAME: air-acetylene, oxidizing

WAVELENGTH: 283.3 nm

BACKGROUND CORRECTION: D_2 or H_2 lamp

CALIBRATION: Pb^{++} in 10% HNO_3

RANGE: 10 to 200 µg per sample [3,8]

ESTIMATED LOD: 2.6 µg per sample [9]

PRECISION (s_r): 0.03 [2]

APPLICABILITY: The working range is 0.025 to 0.5 mg/m³ for a 400-L air sample. The method is applicable to elemental lead, including Pb fume, and all other aerosols containing lead. This is an elemental analysis, not compound specific. Aliquots of the samples can be analyzed separately for additional elements.

INTERFERENCES: Use D_2 or H_2 continuum background correction to control flame or molecular absorption. High concentrations of calcium, sulfate, carbonate, phosphate, iodide, fluoride, or acetate can be corrected.

OTHER METHODS: This method combines and replaces P&CAM 173 [8] and S341 [7,9] for lead. Method 7300 (ICP-AES) is an alternate analytical method.Method 7505 is specific for lead sulfide. The following have not been revised: the dithizone method, which appears in P&CAM 102 [4] and the lead criteria document [1]; P&CAM 191 (ASV) [5]; and P&CAM 214 (graphite furnace-AAS) [6].

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REAGENTS:

1. Nitric acid, conc.
2. Nitric acid, 10% (w/v). Add 100 mL conc. HNO_3 to 500 mL water; dilute to 1 L.
3. Hydrogen peroxide, 30% H_2O_2 (w/w), reagent grade.
4. Calibration stock solution, 1000 µg Pb/mL. Commercial standard or dissolve 1.00 g Pb metal in minimum volume of (1+1) HCl and dilute to 1 L with 1% (v/v) HCl. Store in a polyethylene bottle. Stable ≥ one year.
5. Air, compressed, filtered.
6. Acetylene.
7. Distilled or deionized water.

EQUIPMENT:

1. Sampler: Cellulose ester filter, 0.8-µm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Atomic Absorption Spectrophotometer with an air-acetylene burner head.
4. Lead hollow cathode lamp or electrode dischargeless lamp.
5. Regulators, two-stage, for air and acetylene.
6. Beakers, Phillips, 125 mL, or Griffin, 50 mL with watchglass covers.*
7. Volumetric flasks, 10- and 100-mL.*
8. Assorted volumetric pipets as needed.*
9. Hotplate, surface temperature 140° C.
10. Bottles, polyethylene, 100-mL.

*Clean all glassware with conc. nitric acid and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Perform all acid digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for up to 8 hrs for TWA measurements. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

NOTE: The following sample preparation gave quantitative recovery (see EVALUATION OF METHOD) [9]. Steps 4 through 9 of Method 7300 or other quantitative ashing techniques may be substituted, especially if several metals are to be determined on a single filter.

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
4. Add 3 mL conc. HNO_3, and 1 mL 30% H_2O_2 and cover with a watchglass. Start reagent blanks at this step.
   NOTE: If PbO_2 is not present in the sample, the 30% H_2O_2 need not be added [3,9].
5. Heat on hotplate (140 °C) until most of the acid has evaporated.
6. Repeat two more times using 2 mL conc. HNO_3 and 1 mL 30% H_2O_2 each time.
7. Heat on 140 °C hotplate until a white ash appears.
8. When sample is dry, rinse the watchglass and walls of the beaker with 3 to 5 mL 10% HNO_3. Allow the solution to evaporate to dryness.
9. Cool each beaker and dissolve the residues in 1 mL conc. HNO_3.
10. Transfer the solution quantitatively to a 10-mL volumetric flask and dilute to volume with distilled water.
    NOTE: If the concentration (M) of any of the following is expected to exceed the lead concentration (M) by 10-fold or more, add 1 mL 1 M Na_2EDTA to each flask before dilution to volume: $CO_3^=$, PO_4^{-3}, I^-, F^-, CH_3COO^-. If Ca^{++} or $SO_4^=$ are present in 10-fold excess, make all standards and samples 1% (w/w) in La^{++} [8].

CALIBRATION AND QUALITY CONTROL:

11. Prepare a series of working standards covering the range 1 to 20 µg Pb/mL (1 to 200 µg Pb per sample) by adding aliquots of calibration stock solution to 100-mL volumetric flasks. Dilute to volume with 10% HNO_3. Store the working standards in polyethylene bottles and prepare fresh weekly.
12. Analyze the working standards together with the blanks and samples (steps 17 and 18).
13. Prepare a calibration graph of absorbance vs. solution concentration (µg/mL).
14. Aspirate a standard for every 10 samples to check for instrument drift.
15. Check recoveries with at least one spiked media blank per 10 samples.
16. Use method of additions occasionally to check for interferences.

MEASUREMENT:

17. Set spectrophotometer as specified by the manufacturer and to conditions on page 7082-1.
    NOTE: An alternate wavelength is 217.0 nm [10]. Analyses at 217.0 nm have slightly greater sensitivity, but poorer signal-to-noise ratio compared to 283.3 nm. Also, non-atomic absorption is significantly greater at 217.0 nm, making the use of D_2 or H_2 continuum background correction mandatory at that wavelength.
18. Aspirate standards, samples, and blanks. Record absorbance readings.
    NOTE: If the absorbance values for the samples are above the linear range of the standards, dilute with 10% HNO_3, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

19. Using the measured absorbances, calculate the corresponding concentrations (µg/mL) of lead in the sample, C_s, and average media blank, C_b, from the calibration graph.
20. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration, C (mg/m^3), of lead in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method S241 [7] was issued on October 24, 1975, and validated over the range 0.13 to 0.4 mg/m^3 for a 180-L air sample, using generated atmospheres of lead nitrate [2]. Recovery in the range 18 to 72 µg Pb per sample was 98%, and collection efficiency of 0.8-µm mixed cellulose ester filters (Millipore Type AA) was 100% for the aerosols. Subsequent studies on analytical recovery of 200 µg Pb per sample gave the results [3,9]:

Species	Digestion Method	Analytical Recovery, %
Pb metal	HNO_3 only	92 ± 4
Pb metal	HNO_3 + H_2O_2	103 ± 3
PbO	HNO_3 only	93 ± 4
PbS	HNO_3 only	93 ± 5
PbO_2	HNO_3 only	82 ± 3
PbO_2	HNO_3 + H_2O_2	100 ± 1
Pb in paint*	HNO_3 only	95 ± 6
Pb in paint*	HNO_3 + H_2O_2	95 ± 6

*Standard Reference Material #1579, U.S. National Bureau of Standards.

Additional collection efficiency studies were also done using Gelman GN-4 filters for the collection of Pb fume, which had geometric mean diameter of 0.1 μm [3]. Mean collection efficiency for 24 sampling runs at flow rates between 0.15 and 4.0 L/min was >97 ± 2%. Overall precision, s_r, was 0.072 for lead nitrate aerosol [2,7] and 0.068 for Pb fume [3,9].

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METHOD REVISED BY: Mark Millson and R. DeLon Hull, NIOSH/DPSE; S341 originally validated under NIOSH Contract CDC-94-74-45; additional studies under NIOSH Contract 210-79-0058.

FORMULA: PbS

M.W.: 239.25

LEAD SULFIDE

METHOD: 7505
ISSUED: 2/15/84

OSHA: 0.05 mg (Pb)/m³
NIOSH: 0.1 mg (Pb)/m³ [1]
ACGIH: 0.15 mg (Pb)/m³
(1 mg/m³ Pb = 1.16 mg/m³ PbS)

PROPERTIES: solid; d 7.5 g/mL; MP 1114 °C

SYNONYMS: galena (mineral); CAS# 1314-87-0.

SAMPLING

SAMPLER: CYCLONE + FILTER
(10-mm nylon cyclone + 5-µm PVC membrane)

FLOW RATE: 1.7 L/min

VOL-MIN: 300 L
-MAX: 800 L

SHIPMENT: routine

SAMPLE STABILITY: 4% degradation in 45 days; protect samples from light

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: required; area respirable or settled dust

ACCURACY

RANGE STUDIED: 12 to 37 µg/m³ [2]

BIAS: not significant when samples and standards have equivalent particle size

OVERALL PRECISION (s_r): 0.103 [2]

MEASUREMENT

TECHNIQUE: X-RAY POWDER DIFFRACTION

ANALYTE: lead sulfide

DISSOLVE: filter in tetrahydrofuran

SUSPEND: in tetrahydrofuran

REDEPOSIT: 0.45-µm Ag membrane filter

XRD: Cu target X-ray tube
Optimize for intensity; 1° receiving slit
Graphite monochromator; scintillation detector
Slow step scan, 0.02°/10 sec
Integrated intensity with background subtraction

CALIBRATION: suspensions of PbS in 2-propanol

RANGE: 30 to 2000 µg per sample

ESTIMATED LOD: 3 µg per sample

PRECISION (s_r): 0.081 (40 to 260 µg per sample [2]

APPLICABILITY: The working range is 0.06 to 4 mg/m³ for a 500-L air sample. The method is specific for determining lead sulfide among other mine dusts.

INTERFERENCES: Lead oxide (PbO, Pb_3O_4), lead sulfate (anglesite), copper iron sulfide (chalcopyrite); also see APPENDIX A.

OTHER METHODS: This method was originally designated P&CAM 350, which it replaces [3].

REAGENTS:

1. Lead sulfide, ACS grade, <10-μm particle size.*
   NOTE: Do not use very old lead sulfide (>10 years) because it will probably contain lead sulfate. Perform a qualitative analysis (step 10) to determine the purity of the lead sulfide. The material also must be ultrasonically wet-sieved with a 10-μm pore size sieve to approximate respirable dust. Evaporate the alcohol. Dry the sieved material in an oven at 110 °C for 1 hr, cool and store in a desiccator.
2. 2-Propanol.
3. Tetrahydrofuran (THF).*
4. Desiccant.

*See Special Precautions.

EQUIPMENT:

1. Personal sampler: 10-mm nylon cyclone; polyvinyl chloride (PVC) membrane filter, 37-mm diameter, 5-μm pore size; in plastic filter cassette.
   NOTE: Use FWSB filters (MSA Co). Gelman VM-1; Millipore BS, BD and PVC5; and Glasrock PVC are not sufficiently soluble in THF.
2. Personal sampling pump calibrated to ± 5% at 1.7 L/min, with flexible connecting tubing.
3. High-volume sampler: 0.5-inch HASL cyclone; PVC filter (see 1. above), with high-volume pump, 9 L/min.
4. Silver membrane filters, 25-mm diameter, 0.45-μm pore size (Selas Flotronics, Dresher, PA 19006).
5. X-ray powder diffractometer equipped with copper target X-ray tube, graphite monochromator and scintillation detector.
6. Reference specimen (mica, Arkansas stone or other stable standard) for data normalization.
7. Filtration apparatus and side arm vacuum flask with 25- and 37-mm filter holders.
8. Sieve, 10-μm, for wet-sieving.
9. Analytical balance (0.01 mg); magnetic stirrer; ultrasonic bath or probe; volumetric pipettes and flasks; centrifuge tubes (wide mouth), 40-mL and test tube rack; desiccator; reagent bottles with ground glass stoppers; drying oven; polyethylene wash bottle; Pyrex beakers, 50-mL, and matching watchglasses; and glue or tape for securing Ag filters to XRD holder.

SPECIAL PRECAUTIONS: THF is extremely flammable and should be used in a fume hood.

Avoid inhaling lead sulfide dust [1].

SAMPLING:

1. Calibrate each personal sampling pump to 1.7 L/min with a representative sampler in line.
2. Sample at 1.7 L/min for a total sample size of 300 to 800 L. Do not exceed 2 mg dust loading on the filter.
   NOTE: Do not allow the sampler assembly to be inverted at any time. Turning the cyclone to anything more than a horizontal orientation may deposit oversized material from the cyclone body onto the filter.
3. Take a high-volume respirable dust sample (e.g., 4 m^3 @ 9 L/min).

SAMPLE PREPARATION:

NOTE: Protect the filters from exposure to intense light during storage.

4. Using forceps, place filters in 40-mL wide-mouth centrifuge tubes. Add 10 mL THF to each tube. (The filter dissolves instantly.) Place the centrifuge tubes on the test tube rack in the ultrasonic bath for 10 min.

5. Place a silver filter in the filtration apparatus and attach the funnel. Pour the suspensions from the centrifuge tube into the funnel.
6. Wash the empty centrifuge tube with 5 mL THF and shake tube by hand or by vortex mixer for a few seconds. Transfer the THF to the filtration funnel. Repeat with two more 5-mL portions of THF.
7. Control the filtration rate to keep the liquid level in the funnel near the top during rinsing. Do not wash the walls or add THF to the funnel when the liquid level is lower than 4 cm above the filter. Leave the vacuum on after filtration to produce a dry filter. Remove the filter with forceps and mount it in the XRD sampler holder.

CALIBRATION AND QUALITY CONTROL:

8. Select six silver membrane filters as media blanks randomly from the same box of filters to be used for depositing the samples. These will be used to correct for sample self-absorption. Mount each of the media blanks on the filtration apparatus and apply vacuum to draw 5 to 10 mL of 2-propanol through the filter. Remove, let dry and mount on XRD holders. Determine the net normalized count for the silver peak, $\hat{I}^{o}_{Ag}$, for each media blank (step 11). Average the values for the six media blanks.
9. Prepare and analyze working standard filters.
   a. Prepare two suspensions by weighing 10 and 100 mg of the dry, sieved lead sulfide to the nearest 0.01 mg. Quantitatively transfer each to a 1-L glass-stoppered bottle using 1.00 L 2-propanol.
   b. Suspend the powder in the 2-propanol using an ultrasonic probe or bath for 20 min. Immediately move the flask to a magnetic stirrer with thermally-insulated top and add a stirring bar. Cool to room temperature before use.
   c. Mount a silver filter on the filtration apparatus. Place 2 to 4 mL 2-propanol on the filter. Turn off the stirrer and shake the suspension vigorously by hand. Immediately remove the lid and withdraw an aliquot from the center of the suspension. Do not adjust the volume in the pipet by expelling part of the suspension. If more than the desired aliquot is withdrawn, return all of the suspension to the bottle, rinse, and dry the pipet and take a new aliquot. Transfer the aliquot from the pipet to the filter keeping the tip of the pipet near the surface but not submerged in the delivered suspension.
   d. Rinse the pipet with several mL 2-propanol, draining the rinse into the funnel. Repeat the rinse several more times.
   e. Apply vacuum and rapidly filter the suspension. Leave vacuum on until filter is dry. Do not wash down the sides of the funnel after the deposit is in place since this will rearrange the material on the filter. Transfer the filter to the XRD sample mount. Prepare working standard filters in triplicate by this technique at, e.g., 30, 50, 100, 200, 500, 1000, and 2000 µg lead sulfide.
   f. Analyze by XRD (step 11). Use the same diffraction peaks and instrumental conditions as for samples. Designate the net and normalized XRD intensities for the working standard filters as I^{o}_{x} (step 11.d) and $\hat{I}^{o}_{x}$ (step 11.e), respectively. Correct $\hat{I}^{o}_{x}$ for matrix absorption for standards containing more than 200 µg PbS (steps 11.f and 12).
   g. Prepare a calibration graph by plotting $\hat{I}^{o}_{x}$ vs. mass PbS (µg). A weighted least squares ($1/\sigma^2$) fit is preferable.
   h. Determine the slope, m (counts/µg), of the calibration graph. The intercept of the line should be zero $\pm$ 5 µg.

MEASUREMENT:

10. Obtain a qualitative X-ray diffraction scan (e.g., 10 to 80° 2-θ) of the settled dust bulk or high-volume respirable sample to determine the presence of lead sulfide and any matrix interference (see APPENDIX). If quantitative analysis is to be performed on the field bulk (percent PbS), wet-sieve it through a 10-μm sieve in order to match the particle size of the standards. The expected diffraction peaks are:

	Peak (2-θ Degrees)	
	Primary	Secondary
Lead Sulfide	30.10°	25.98°
Silver	38.12°	44.28°

11. Mount the filter (sample, standard or blank) in the XRD instrument and:
    a. Determine the net intensity, I_r, of the reference specimen before each filter is scanned. Select a convenient normalization scale factor, N, which is approximately equivalent to the net count for the reference specimen peak and use this value of N for all analyses.
    b. Measure the diffraction peak area of the most intense interference-free diffraction peak of PbS. Scan times must be long, e.g., 15 min.
    c. Measure the background on each side of the peak for one-half the time used for peak scanning. Add the counts from each side to obtain a total (average) background. Determine the position of the background for each sample.
    d. Calculate the net intensity, I_x (the difference between the peak integrated count and the total background count).
    e. Calculate the normalized intensity, $\hat{I}_x$, for the sample peak on each sample, field blank and standard:

$$\hat{I}_x = \frac{I_x}{I_r} \cdot N.$$

    NOTE: Normalizing to the reference specimen intensity compensates for long-term drift in X-ray tube intensity. If intensity measurements are stable, the reference specimen may be run less frequently and the net intensities should be normalized to the most recently measured reference intensity.
    f. Determine the net count, I_{Ag}, of an interference-free silver peak on the sample filter following the same procedure. Use a short scan time for the silver peak (e.g., 5% of scan time for analyte peaks) throughout the method.
    g. Scan each field blank over the same 2-θ range used for PbS and silver peaks. These analyses serve only to verify that contamination of the filters has not occurred. The analyte peak should be absent. The normalized intensity of the silver peak should match that of the media blanks.

CALCULATIONS:

12. Calculate the concentration of lead sulfide, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{\hat{I}_x \cdot f(T) - b}{m \cdot V}, \ mg/m^3.$$

where: $\hat{I}_x$ = normalized intensity for sample peak

b = intercept of calibration curve ($\hat{I}^0_x$ vs. W)

m = initial slope of calibration curve, counts µg

$f(T) = \frac{-R \ln T}{1 - T^R}$ = absorption correction factor (Table 1)

$R = \sin(\Theta_{Ag})/\sin(\Theta_x)$

$T = \hat{I}_{Ag}/(\text{average } \hat{I}^0_{Ag})$ = transmittance of sample

$\hat{I}_{Ag}$ = normalized silver peak intensity from sample

average $\hat{I}_{Ag}$ = normalized silver peak intensity from media blanks (average of six values)

NOTE: For a more detailed discussion of the absorption correction procedure, see references [4] and [5].

EVALUATION OF METHOD:

The measurement precision, s_r, initially determined with 30 samples in the range 30 to 2000 µg PbS per filter was 0.047 [6]. The same 30 samples plus five blank filters were analyzed by X-ray fluorescence for lead and sulfur and by ICP-AES for lead in order to verify the accuracy of the PbS filter depositions. A recovery study with 20 spiked samples in the range of 30 to 150 µg PbS per filter indicated a 102.6% average recovery and a 0.05 relative standard deviation.

Another recent study [2] involving 54 spiked samples in the range 40 to 250 µg PbS per filter indicated an 0.081 precision and a 98% recovery. The overall method was also evaluated in the study using eight sets of samples collected in galena mills. A set consisted of six filters collected side by side. Average PbS in air concentrations for these sets ranged from 12 to 35 µg/m^3 and the pooled s_r for seven of these averages was 0.103. The eighth set was an outlier [2].

Two stability studies [6] were performed: a short-term (47 days) and a long-term (6.5 months). In the short-term study, 15 PbS samples were exposed to various conditions from intense light to no light, from moist air to vacuum; all were analyzed at intervals. During analysis, they were all subjected to a total of over 2 hrs exposure to X-ray radiation at 1400 watts. Under continuous intense light, the PbS degradation was 14.4%. The smallest degradations were with no light (1.2 to 3.8%). In the long-term study, a PbS bulk sample exposed to ambient laboratory air and light conditions and a total of 36 hrs of X-ray radiation degraded 37.6%. A filter similarly exposed in the lab for 158 days and a total of 28 hrs of X-radiation degraded 12.2%. It is, therefore, recommended that the samples be protected from light.

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METHOD WRITTEN BY: J. Palassis, M. T. Abell, D. D. Dollberg, Ph.D. and M. Hawkins, NIOSH/DPSE.

APPENDIX:

INTERFERENCES

If interferences are present, use a different lead sulfide peak. Lead oxide (PbO yellow-form), lead sulfate (anglesite) and copper iron sulfide ($CuFeS_2$ chalcopyrite) interfere with the primary lead sulfide peak, using copper Kα X-ray radiation. Lead oxide (Pb_3O_4 orange-form) and lead sulfate (anglesite) also interfere with the secondary lead sulfide peak. The oxides of lead do not occur naturally in appreciable amounts in galena mining but are formed when lead sulfide is heated at high temperatures (i.e., in smelting and roasting operations) [7]. Dolomite, zinc sulfide (ZnS sphalerite) and chalcopyrite that are normally found in galena mining do not interfere with the secondary lead sulfide peak; for this reason the secondary lead sulfide peak was chosen as the analytical peak. The tertiary lead sulfide peak interferes with the secondary silver peak.

When peak overlaps are not severe, a smaller receiving slit or chromium X-radiation may be used; however, a new calibration curve will be necessary.

The presence of some elements in the sample (iron, in particular) can result in appreciable X-ray fluorescence, leading to high background intensity. This can be minimized by a diffracted beam monochromator.

The interfering effects of X-ray absorption by the sample result in attenuation of the diffracted beam and correction must be made (step 12 and Table 1).

Table 1. Matrix absorption correction factors for lead sulfide/silver peaks, degrees 2θ.

Lead Sulfide		30.10	25.98		30.10	25.98
Silver		38.12	38.12		38.12	38.12
	T	f(T)	f(T)	T	f(T)	f(T)
	1.00	1.0000	1.0000	0.74	1.2013	1.2346
	0.99	1.0063	1.0073	0.73	1.2109	1.2460
	0.98	1.0128	1.0147	0.72	1.2208	1.2575
	0.97	1.0193	1.0223	0.71	1.2308	1.2693
	0.96	1.0259	1.0299	0.70	1.2410	1.2814
	0.95	1.0326	1.0377	0.69	1.2514	1.2936
	0.94	1.0394	1.0456	0.68	1.2620	1.3062
	0.93	1.0463	1.0536	0.67	1.2729	1.3190
	0.92	1.0533	1.0618	0.66	1.2839	1.3320
	0.91	1.0605	1.0701	0.65	1.2952	1.3453
	0.90	1.0677	1.0785	0.64	1.3067	1.3590
	0.89	1.0751	1.0870	0.63	1.3185	1.3729
	0.88	1.0825	1.0957	0.62	1.3305	1.3871
	0.87	1.0901	1.1046	0.61	1.3428	1.4017
	0.86	1.0978	1.1136	0.60	1.3554	1.4165
	0.85	1.1057	1.1227	0.59	1.3682	1.4318
	0.84	1.1136	1.1320	0.58	1.3813	1.4473
	0.83	1.1217	1.1414	0.57	1.3948	1.4633
	0.82	1.1300	1.1511	0.56	1.4085	1.4796
	0.81	1.1383	1.1609	0.55	1.4226	1.4963
	0.80	1.1469	1.1708	0.54	1.4370	1.5135
	0.79	1.1555	1.1810	0.53	1.4518	1.5311
	0.78	1.1644	1.1913	0.52	1.4669	1.5491
	0.77	1.1733	1.2018	0.51	1.4825	1.5676
	0.76	1.1825	1.2126	0.50	1.4984	1.5866
	0.75	1.1918	1.2235	0.49	1.5148	1.6061

T = sample transmittance (step 12).
f(T) = sample correction factor (step 12).

FORMULA: Hg

M.W.: 200.59

MERCURY

METHOD: 6000
ISSUED: 2/15/84

OSHA: 0.1 mg/m³
NIOSH: 0.05 mg/m³ [1]
ACGIH: 0.05 mg/m³

PROPERTIES: liquid; d 13.55 g/mL @ 20 °C;
BP 356 °C; MP -39 °C;
VP 0.16 Pa (0.0012 mm Hg; 13.2 mg/m³) @ 20 °C

SYNONYMS: quicksilver; CAS# 7439-97-6.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(30 mg silvered Chromosorb P, with glass fiber prefilter)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 0.5 L
-MAX: 7 L @ 0.1 mg/m³

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days @ 25 °C [2]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.0456 to 0.18 mg/m³ [2,4] (3-L samples)

BIAS: not significant [2,4]

OVERALL PRECISION (s_r): 0.061 [2]

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, FLAMELESS

ANALYTE: elemental mercury

DESORPTION: thermal (650 to 700 °C)

CARRIER GAS: air, 1.0 L/min

WAVELENGTH: 253.7 nm

CALIBRATION: aqueous Hg^{2+} spikes onto sampler

RANGE: 0.01 to 1 µg per sample [2,4]

ESTIMATED LOD: 0.001 µg per sample

PRECISION (s_r): 0.051 [2,3]

APPLICABILITY: The working range is 0.003 to 0.3 mg/m³ for a 3-L air sample. If a glass fiber (13-mm) filter is used to prevent potential interference from mercury compounds, this filter may be analyzed for particulate Hg species [4]. This method is not affected by high humidity environments (breakthrough determined at 85% R.H.) [2].

INTERFERENCES: Chlorine and other strong oxidizing gases which attack silver (the sampling substrate), reduce the efficiency of the sampling tube but do not interfere in the measurement. Methyl mercuric chloride is partially retained on the sampler and is, therefore, a potential interferent [5].

OTHER METHODS: This method combines and replaces P&CAM 175 [4] and S199 [3].

REAGENTS:

1. Mercury standard, 1000 µg/mL. Commercially available or dissolve 1.35 g mercuric chloride in 10 mL conc. HNO_3; dilute to 1.0 L with deionized water.
2. Mercury standard, 10 µg/mL. Dilute 1.0 mL 1000 µg/mL stock solution and 1.0 mL conc. HNO_3 to 100 mL with deionized water.
3. Mercury standard, 1.0 µg/mL. Dilute 0.1 mL 1000 µg/mL stock solution and 1.0 mL conc. HNO_3 to 100 mL with deionized water.
4. Nitric acid, conc.
5. Water, deionized.

EQUIPMENT:

1. Sampler: glass tube, 2 cm long, 6 mm OD, 4 mm ID, unsealed ends containing one section of 30 mg silvered Chromosorb P (AgCP) held in place with quartz wool plugs (commercially available); preceded by a prefilter unit (13-mm glass fiber filter in cassette filter holder).
   NOTE: A 37-mm, 0.8-µm cellulose pre-ester filter may be used if determination of particulate Hg is not desired.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Thermal desorption unit (see APPENDIX).
4. Atomic absorption spectrophotometer, cold-vapor, with Hg lamp, with 2.5- to 4-cm path length gas cell.
5. Volumetric flasks, 100-mL.*
6. Micropipets, 10- to 100-µL.*
7. Tape, PTFE.
8. Gloves, lint-free.

*Clean all glassware with conc. nitric acid and rinse thoroughly with deionized water before use.

SPECIAL PRECAUTIONS: Mercury is readily absorbed by inhalation and intact skin [1]. Vacuum pump of the thermal desorption system should be vented into a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove the sampler from its storage vial and attach it to a personal sampling pump with flexible tubing. Wrap the sampler tube with PTFE tape to protect the outside of the tube from contamination.
   NOTE: Handle the sampler only with clean lint-free gloves or tissues to prevent contamination.
3. Sample at 0.01 to 0.2 L/min. Do not exceed a sample volume of 7 L if the concentrations are at or above the OSHA standard.
4. Remove the PTFE tape and return the sampler to its storage vial after sampling being careful not to contaminate the outside of the tube.

SAMPLE PREPARATION: None required.

CALIBRATION AND QUALITY CONTROL:

5. Prepare at least five working standards by adding known amounts of 1 µg/mL or 10 µg/mL mercury standard covering the range 0.01 to 1 µg Hg per sample to unused AgCP sampler tubes.
6. Analyze the working standards together with the samples and blanks (steps 8 through 12).
7. Prepare calibration graph of absorbance vs. µg Hg per tube.

MEASUREMENT:

8. Set up the measurement system as described in the APPENDIX.
9. Purge the system before analyzing samples and standards by heating the first desorption section 60 sec, allowing to cool 60 sec and heating second section 30 sec.
10. Allow system to cool 1 min before analyzing samples.
11. Measure samples and standards by inserting the tube, thermally desorbing first section 60 sec, waiting 60 sec and desorbing second section for 30 sec.
    NOTE: Handle the tube only with lint-free gloves or tissues to prevent contamination.
12. Allow the system to cool at least 30 sec before removing tube and inserting the next sample.
    CAUTION: Tubes are hot when removed. Catch them in a dry beaker as they come out of the desorption unit.

CALCULATIONS:

13. Read the absorbance of the sample and calculate the mass of Hg on the samples, W (µg), and blanks from the calibration graph. Obtain an average value for the media blanks, B (µg).
14. Calculate the concentration, C (mg/m^3), of mercury in air volume sampled, V (L):

$$C = \frac{W - B}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method S199 [2] was issued on July 8, 1977, and validated over the range 0.046 to 0.18 mg/m^3 at 760 mm Hg and 18.0 °C using a 3-L sample [6]. Overall precision, s_r, was 0.061 with average recovery of 100.7%. The mercury concentration was independently determined by theoretical calculations based on mercury vapor pressure data and flow rate. Breakthrough did not occur after sampling 3.5 hrs at 0.184 L/min (39 L) in a Hg concentration of 0.244 mg/m^3 and 85% relative humidity. Six samples stored at room temperature for seven days gave results not significantly different from samples that were analyzed immediately after exposure.

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Inorganic Mercury, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 73-11024 (1973).
[2] Backup Data Report No. S199, prepared under NIOSH Contract 210-76-0123, available as "Ten NIOSH Analytical Methods, Set 5," available as Order No. PB 287-499 from NTIS, Springfield, VA 22161 (1977).
[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, S199, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[4] Ibid, V. 5, P&CAM 175, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[5] Trujillo, P. E. and E. E. Campbell. Development of a Multistage Air Sampler for Mercury, Anal. Chem., 47, 1629-1634 (1975).
[6] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY: R. DeLon Hull, NIOSH/DPSE; S199 originally validated under NIOSH Contract CDC-99-76-123.

APPENDIX:

MERCURY MEASUREMENT SYSTEM

A. Thermal Desorption Unit. With the exception of the electrical components and the loading spring, the entire thermal desorption unit is made of either quartz or Pyrex glass. Descriptions of each important part of the thermal desorption unit numbered in Figure 6000-2 are as follows:

1-2. Loading mechanism (Figure 6000-2). Made from a glass 18/7 female standard socket joint with steel spring (#1) and a plunger tube (3-mm or 4-mm OD quartz - #2). The length of the plunger is cut to reach the sample desorption section.
3. Rubber or neoprene "O" rings for holding quartz desorption tube in place.
4. Sample desorption section. Made from 8-mm ID and 5-mm ID quartz tubing. The junction between the two sizes of tubing is tapered on the inside so that sampling tube tips fit snugly against the junction.
5. Cooling vent holes. Seven 4-mm holes in the outer jacket to vent the cooling air.
6. Sampler tube. Held in position for desorption by the spring on the loading mechanism.
7. Sample desorption coils. Twenty-eight coils of 18-gauge nichrome wire around the sample desorption section.
8. Quartz wool plugs. Used to separate each section. Although the plugs should be large enough to hold the materials, they should not be packed too tightly.
9. Cupric oxide (CuO). A 40-mm section of rod-shaped CuO, retained by a dimple in the tubing and quartz wool plug placed just downstream from the sampling tubes. When heated, the CuO oxidizes organic vapors desorbed from the sampler.
10. Cooling jacket. Pyrex glass; directs the flow of cooling air and acts as electrical insulation for the heating coils.
11. Second desorption section. Five-mm ID quartz tubing extending from the first desorption section. The contents are held in place by a dimple in the glass tube.
12. Gold section desorption coils. Thirty coils of 20-gauge nichrome wire concentrated over the gold section. The gold section is a 25-mm length of powdered gold, mixed 1:1 with 20/40 mesh sea sand to prevent fusing of the gold granules and to facilitate airflow.
13. Cooling air intake. Six-mm ID glass tubing, connected to the cooling air supply.
14. Wire lead-throughs and solderless connectors. Wires enter the cooling jacket through 5-mm holes at the ends of glass nipples on the jacket with solderless connectors between the wires and the coils. The wires are held in place with a heat resistant sealant.
15. Outlet. Butt-connected with PVC tubing overseal to a glass tube which leads to the detection system. The end of the quartz tube fits through the end of the cooling jacket with minimum clearance to limit loss of cooling air.

B. Electrical Power (Figure 6000-1). The wires to the heating coils should be heavy enough (about #12) to carry the current necessary to heat the coils. Power to the heating coils is controlled by a three-position switch with an off position, an on position for the sample desorption section and on position for the gold section. Power to the switch comes from a 120 V ac Input, 20 A variable transformer set between 20 and 30 V ac. The exact setting is determined by testing the thermal desorption unit for complete desorption of mercury from the sample tube in one heating. Complete desorption usually occurs when the sample tube reaches a maximum of 650 °C. The time required for heating may vary slightly from that stated in the method (60 sec) due to the spacing between heating coils and the concentration of heat near the sample tube and/or desorption sections.

C. Carrier Air Supply. Room air is drawn by vacuum pump, attached to a ballast tank to prevent fluctuations in airflow.

Before entering the desorption unit, the air passes through a drying tube containing anhydrous $Mg(ClO_4)_2$ or other suitable drying agent. The dimensions of the drying tube and subsequent filters are not critical but should not impede airflow. Change the drying agent periodically, depending on the humidity of the air. The dried air passes through a filter containing activated charcoal and 30/60 mesh silvered Chromosorb P or Mersorb charcoal to remove organic vapors and metallic mercury before entering the thermal desorption unit.

Carrier air passes through, in order, the thermal desorption unit, the detection system, a second filter containing Mersorb charcoal which collects the mercury, a 0 to 5 L/min flowmeter, critical orifice, and into the ballast tank of the vacuum pump.

D. Cooling air. Supplied by an air compressor at a flow rate of 20 L/min. The air enters the desorption unit near the second desorption section.

E. Detection system. Mercury from the outlet of the thermal desorption unit enters the optical cell of a flameless atomic absorption spectrophotometer through a glass tube maintained at 70 °C using a heating tape. Power for the heating tape is supplied by a 120 V ac, 8 A variable transformer.

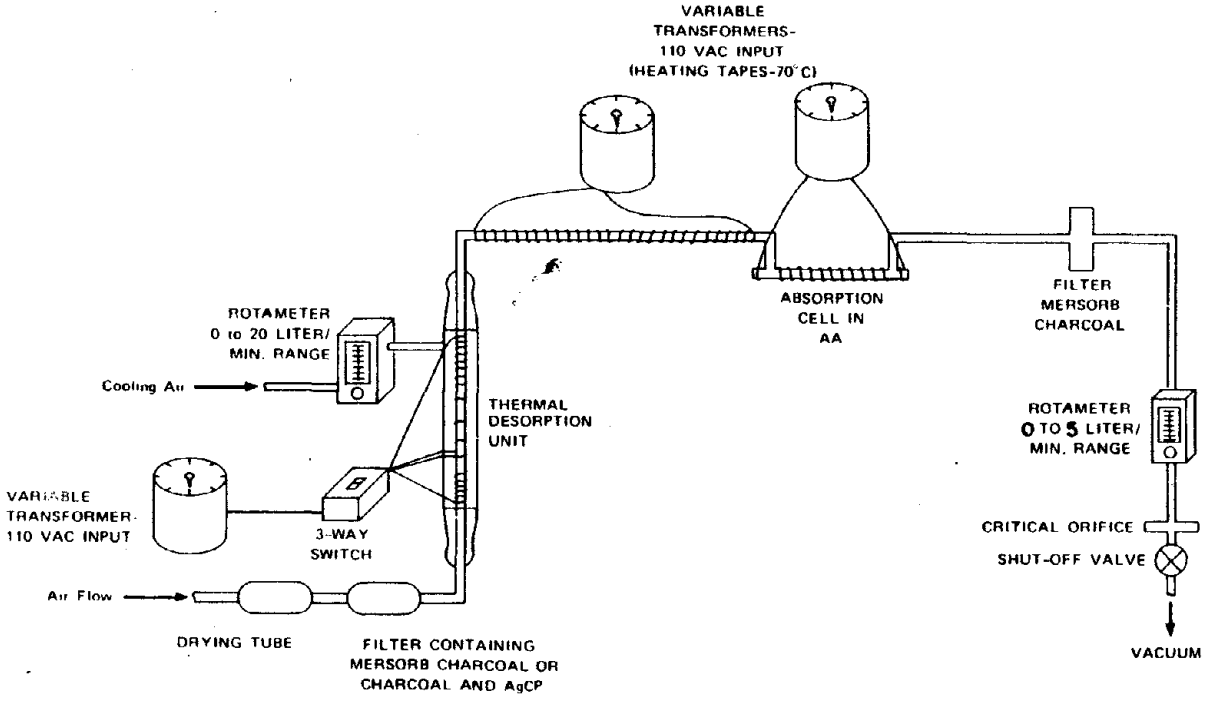
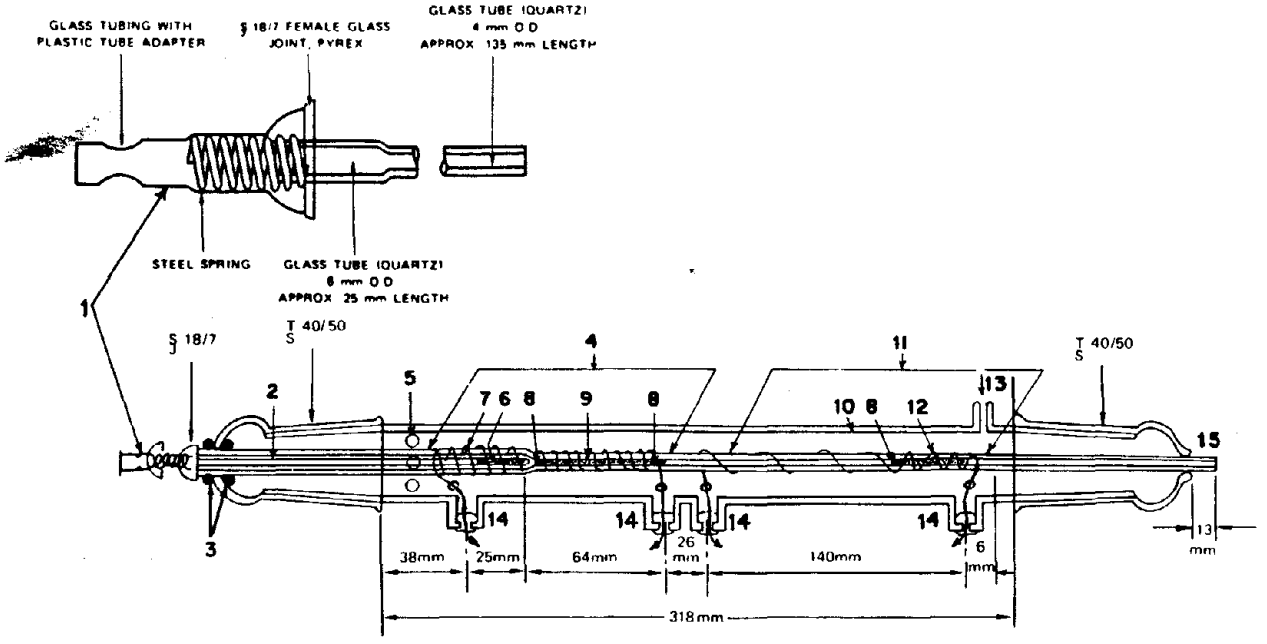


Figure 6000-1 MERCURY ANALYSIS SYSTEM



1. LOADING MECHANISM
2. QUARTZ GLASS PLUNGER TUBE
3. RUBBER "O" RINGS
4. SAMPLE DESORPTION SECTION
5. COOLING AIR VENT HOLES
6. SAMPLING TUBE
7. NICHROME WIRE COILS
8. QUARTZ GLASS WOOL PLUGS
9. CUPRIC OXIDE (CuO)
10. COOLING JACKET
11. SECOND DESORPTION SECTION
12. GOLD SECTION
13. COOLING AIR INTAKE
14. WIRE HOLES AND SOLDERLESS CONNECTORS
15. OUTLET

Figure 6000-2 THERMAL DESORPTION UNIT

FORMULA: CH_3OH; CH_4O

M.W.: 32.04

METHANOL

METHOD: 2000
ISSUED: 2/15/84

OSHA: 200 ppm
NIOSH: 200 ppm; 800 ppm/15 min [1]
ACGIH: 200 ppm; STEL 250 ppm
(1 ppm = 1.310 mg/m³ @ NTP)

PROPERTIES: liquid; BP 64.5 °C;
d 0.792 g/mL @ 20 °C;
VP 15.3 kPa (115 mm Hg; 15.1% v/v) @ 20 °C;
explosive range 6 to 36% v/v in air

SYNONYMS: carbinol; methyl alcohol; wood alcohol; CAS #67-56-1.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(silica gel, 100 mg/50 mg)

FLOW RATE: 0.02 to 0.2 L/min

VOL-MIN: 1 L @ 200 ppm
-MAX: 5 L

SHIPMENT: routine

SAMPLE STABILITY: 6 weeks

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: desirable, 1 to 10 mL

ACCURACY

RANGE STUDIED: 140 to 540 mg/m³ [2]
(5-L samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.063 [2]

MEASUREMENT

!
!TECHNIQUE: GAS CHROMATOGRAPHY, FID
!
!ANALYTE: methanol
!
!DESORPTION: 1 mL water; stand 4 hrs
!
!INJECTION VOLUME: 5 µL
!
!TEMPERATURE-INJECTION: 200 °C
! -DETECTOR: 250 - 300 °C
! -COLUMN: 80 °C
!
!CARRIER GAS: N_2 or He, 30 mL/min
!
!COLUMN: glass, 2 m x 2 mm ID, 60/80 mesh
! Tenax GC or equivalent
!
!CALIBRATION: solutions of methanol in water
!
!RANGE: 0.1 to 6 mg per sample
!
!ESTIMATED LOD: 0.01 mg per sample [5]
!
!PRECISION (s_r): 0.032 [2]
!
!

APPLICABILITY: The working range is 25 to 900 mg/m³ (19 to 690 ppm) for a 5-L air sample. The method is applicable to ceiling determinations. At high concentrations of methanol or at high relative humidity, a large silica gel tube is required (700 mg front section).

INTERFERENCES: None identified. Positive identification by mass spectrometry may be necessary in some cases. Alternative gas chromatographic columns, e.g., SP 1000, SP-2100 or FFAP are also confirmation aids. High relative humidity drastically decreases the capacity of the sampler.

OTHER METHODS: This method combines and replaces Methods S59 [3] and P&CAM 247 [4].

Preceding page blank 339

REAGENTS:

1. Water, distilled.
2. Methanol.*
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, filtered.

*See special precautions.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 4 mm ID, containing two sections of 20/40 mesh silica gel separated by a 2-mm portion of urethane foam (front = 100 mg, back = 50 mg).
   NOTE: At high relative humidity or high methanol concentrations, use a larger tube: 15 cm long, 8 mm ID, with three sections of silica gel (700 mg, 150 mg, 150 mg).
2. Personal sampling pump, 0.02 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 2000-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Methanol is flammable and a dangerous fire and explosion risk. It is moderately toxic by ingestion and inhalation.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.02 and 0.2 L/min for a total sample size of 1 to 5 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL distilled water to each vial. Attach crimp cap to each vial.
7. Allow to stand 4 hrs with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.01 to 6 mg methanol per sample.
   a. Add known amounts of methanol to distilled water in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg methanol).
9. Determine desorption efficiency (DE) at least once for each lot of silica gel used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of methanol directly onto front sorbent section with a microliter syringe.

c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg methanol recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2000-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with distilled water, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of methanol found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of methanol in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD

Method S59 [3]was issued on January 17, 1975, and validated over the range 140 to 540 mg/m^3 at 25 °C and 758 mm Hg, using 5-L samples [2]. Overall precision, s_r, was 0.063 with average recovery for 18 samples 94.2%, representing a non-significant bias. The atmospheres were generated by calibrated syringe pump. Desorption efficiency was 0.92 at 1.3 mg methanol and 0.84 at 0.65 mg methanol per sample. Breakthrough (5% on back section) occurred at 52 min when sampling an atmosphere containing 541 mg/m^3 in dry air at 0.2 L/min.

Additional data were gathered using a larger (700 mg front section) silica gel tube under high humidity conditions; these were published in P&CAM 247 [4]. A comparison of the data is consistent with a recommended maximum sample volume of 5 L.

Method	Front Section, mg charcoal	Test Conditions mg/m^3	Test Conditions % RH	Breakthrough Capacity, mg methanol	Breakthrough V, L
S59 [2,3]	100	540	0	5.6	10.4
P&CAM 247 [4]	700	534	85	4.6	8.75

REFERENCES:
[1] Criteria for a Recommended Standard...Occupational Exposure to Methyl Alcohol, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 767-148 (1976).
[2] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[3] NIOSH Manual of Analytical Methods, V. 2, S59, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[4] Ibid, V. 1, P&CAM 247, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[5] User check, UBTL, NIOSH Sequence #4121-K (unpublished, November 3, 1983).

METHOD REVISED BY: Charles Neumeister, NIOSH/DPSE; S59 originally validated under NIOSH Contract CDC-99-74-45.

FORMULA: CH_2Cl_2

METHYLENE CHLORIDE

METHOD: 1005
M.W.: 84.94
ISSUED: 2/15/84

OSHA: 500 ppm; C 1000 ppm; P 2000 ppm
NIOSH: 75 ppm; 500 ppm/15 min [1]
ACGIH: 100 ppm; STEL 500 ppm
(1 ppm = 3.47 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.323 g/mL @ 20 °C;
BP 40 °C; MP -95 °C;
VP 47 kPa (349 mm Hg; 46% v/v) @ 20 °C;
not flammable

SYNONYMS: dichloromethane; CAS #75-09-2.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(2 coconut shell charcoal tubes,
100 mg and 50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 0.5 L @ 500 ppm
-MAX: 2.5 L

SHIPMENT: separate front and backup tubes

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1700 to 7097 mg/m³
(1-L samples) [4]

BIAS: not significant [4]

OVERALL PRECISION (s_r): 0.073 [4]

MEASUREMENT

!
!TECHNIQUE: GAS CHROMATOGRAPHY, FID
!
!ANALYTE: methylene chloride
!
!DESORPTION: 1 mL CS_2, stand 30 min
!
!INJECTION VOLUME: 5 µL
!
!TEMPERATURE-INJECTION: 200 to 225 °C
! -DETECTOR: 250 °C
! -COLUMN: 60 to 90 °C
!
!CARRIER GAS: N_2 or He, 30 mL/min
!
!COLUMN: 3 m x 3 mm stainless steel, 10% SP-1000
! on 80/100 mesh Supelcoport
!
!CALIBRATION: CH_2Cl_2 solutions in CS_2 with
! decane as internal standard
!
!RANGE: 0.3 to 10 mg per sample [3]
!
!ESTIMATED LOD: 0.01 mg per sample [2,5]
!
!PRECISION (s_r): 0.026 [4]
!

APPLICABILITY: The working range is 350 to 10,400 mg/m³ for a 1-L air sample. The method is applicable to ceiling determinations.

INTERFERENCES: None identified. The method was validated using a 6 m x 3 mm stainless steel column packed with 10% FFAP on 100/120 mesh Supelcoport. Alternate chromatographic columns are 10% TCEP on 80/100 Chromosorb PAW, SP-2100, SP-2100 with 0.1% Carbowax 1500, or DB-1 fused silica capillary column.

OTHER METHODS: This is Method S329 [3] in a revised format. This method combines and replaces S329, P&CAM 127 [2], and the criteria document method [1].

REAGENTS:

1. Eluent: carbon disulfide*, chromatographic quality, containing 0.1% v/v decane, benzene or other suitable internal standard.
2. Methylene chloride.
3. Nitrogen or helium, purified.
4. Hydrogen, prepurified.
5. Air, filtered, compressed.

*See Special Precautions.

EQUIPMENT:

1. Sampler: separate front and backup glass tubes, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg). A silylated glass wool plug is placed at each end of each tube. Pressure drop across the tubes at 1 L/min airflow must be less than 3.4 kPa.
   Note: Two commercially-available tubes, each containing 150 mg charcoal in two beds, may be used.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 1005-1).
4. Vials, 2-mL, PTFE-lined caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Connect the two sorbent tubes with a short piece of flexible tubing. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 0.5 to 2.5 L.
4. Separate the front and backup tubes and cap each tube with plastic (not rubber) caps. This prevents migration of methylene chloride between sorbent sections. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.01 to 10 mg methylene chloride per sample.
   a. Add known amounts of methylene chloride to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg methylene chloride).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.

a. Remove and discard back sorbent section of a media blank sampler.
b. Inject a known amount of methylene chloride directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg methylene chloride recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1005-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of methylene chloride found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of methylene chloride in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method S329 [3] was issued on June 6, 1975, and validated over the range 1700 to 7100 mg/m^3 at 25 °C and 763 mm Hg using a 1-L sample [4]. Overall precision, s_r, was 0.073 with average recovery 95.3%, representing a non-significant bias. The concentration of methylene chloride was independently verified by calibrated syringe pump. Desorption efficiency was 0.97 in the range 1.3 mg to 5.3 mg methylene chloride per sample. Breakthrough (5% on back section) occurred at 18.5 min when sampling an atmosphere containing 6726 mg/m^3 methylene chloride at 0.187 L/min at 0% RH.

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Methylene Chloride, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-138 (1976).
[2] NIOSH Manual of Analytical Methods, 2nd ed., V. 1, P&CAM 127, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[3] Ibid, V. 3, S329, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[4] Documentation of the NIOSH Validation Tests, NIOSH, S329, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[5] User check, UBTL, NIOSH Sequence #3990-R (unpublished, November 3, 1983).

METHOD REVISED BY: G. David Foley; Y. T. Gagnon; and K. J. Williams, NIOSH/DPSE; S329 originally validated under NIOSH Contract CDC-99-74-45.

MEVINPHOS

FORMULA: $(CH_3O)_2PO_2C(CH_3)=CHC(O)OCH_3$; $C_7H_{13}O_6P$
M.W.: 224.17

METHOD: 2503
ISSUED: 2/15/84

OSHA: 0.01 ppm (skin)
NIOSH: Group I Pesticide [1]
ACGIH: 0.1 mg/m³ (skin); 0.3 mg/m³ STEL
(1 ppm = 9.16 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.25 g/mL @ 20 °C
BP 325 °C; MP 20.6 °C;
VP 0.4 Pa (0.003 mm Hg; 4 ppm) @ 20 °C

SYNONYMS: dimethyl 2-methoxycarbonyl-1-methylethenyl phosphate; Phosdrin; CAS #7786-34-7.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(extracted Chromosorb 102,
100 mg/50 mg)

FLOW RATE: 0.2 to 1 L/min

VOL-MIN: 15 L
-MAX: 240 L

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days @ 25 °C [2]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.027 to 0.145 mg/m³ [2]
(260-L samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.069 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FPD

ANALYTE: phosphorus

DESORPTION: 1 mL toluene; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 190 °C
-DETECTOR: 215 °C
-COLUMN: 170 °C

CARRIER GAS: N_2 or He, 28 mL/min

COLUMN: 2 m x 2 mm glass; Super-Pak 20M or
equivalent

CALIBRATION: Mevinphos in toluene

RANGE: 5 to 55 µg per sample [2]

ESTIMATED LOD: 0.2 µg per sample [2]

PRECISION (s_r): 0.035 [2]

APPLICABILITY: The working range is 0.003 to 0.03 ppm (0.025 to 0.28 mg/m³) for a 200-L air sample. The method can measure a STEL concentration of < 0.4 mg/m³.

INTERFERENCES: None identified.

OTHER METHODS: This is Method S296 [3] in a revised format.

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REAGENTS:

1. Mevinphos, analytical grade.*
2. Toluene, reagent grade.
3. Calibration stock solution, 5 mg/mL. Dilute 50 mg of Mevinphos to 10 mL with toluene. Prepare in duplicate.
4. Helium, purified.
5. Hydrogen, prepurified.
6. Air, filtered.
7. Extracted resin. Chromosorb 102 20/40 mesh (Johns Manville Corp. or equivalent) extracted in Soxhlet apparatus with 1:1 methanol:acetone solution for 2 hrs and dried at 115 °C under vacuum for 1 hr.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 10-cm long, 8-mm OD, 6-mm ID, flame sealed ends containing two sections of extracted resin (front = 100 mg; back = 50 mg) separated and retained by silylated glass wool plugs. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.2 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame photometric detector with phosphorus filter, integrator and column (page 2503-1).
3. Vials, 2-mL, PTFE-lined caps.
4. Syringes, 1- to 100-µL.
5. Volumetric flasks, 10-mL.
6. Pipet, 1-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Mevinphos is a cholinesterase inhibitor and can be absorbed through the skin. Wear protective gloves and suitable protective clothing when handling the pure material [1].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.2 and 1 L/min for a total sample size of 15 to 240 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL toluene to each vial. Attach cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.2 to 55 µg Mevinphos per sample.
   a. Add known amounts of calibration stock solution to toluene in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. µg Mevinphos).
9. Determine desorption efficiency (DE) at least once for each batch of Chromosorb 102 used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.

c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. µg Mevinphos recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2503-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with toluene, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE) of Mevinphos found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of Mevinphos in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S296 [3] was issued on July 6, 1979, and validated over the range 0.027 to 0.145 mg/m³ at 25 °C using a 240-L sample [2,4]. Overall precision, s_r was 0.0694 with an average recovery of 103.9%, representing a non-significant bias. The concentration of Mevinphos was independently verified by sampling the generator with toluene-filled bubblers and measurement by GC/FPD. Desorption efficiency was 1.04 in the range 7.0 µg to 40.0 µg per sample. After sampling an atmosphere containing 0.195 µg/m³ at 1.0 L/min at 80% RH for 376 min, only 0.6% breakthrough was reported [2].

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure During the Manufacture and Formulation of Pesticides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-174 (1978).
[2] Backup Data Report No. S296, Phosdrin, prepared under NIOSH Contract No. 210-76-0123 (July, 1979), available as Order No. PB 81-228983 from NTIS, Springfield, VA 22161.
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 6, S296, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).
[4] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY: Eugene R. Kennedy, Ph.D., NIOSH/DPSE; S296 originally validated under NIOSH Contract No. 210-76-0123.

FORMULA: Table 1

M.W.: Table 1

NAPHTHAS

METHOD: 1550
ISSUED: 2/15/84

OSHA/NIOSH/ACGIH: Table 1

PROPERTIES: Table 1

SYNONYMS: Petroleum ether (benzin), rubber solvent, petroleum naphtha, VM&P naphtha (CAS #8030-30-6), mineral spirits, Stoddard solvent (CAS #8052-41-3), kerosene (kerosine), coal tar naphtha.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1.3 L @ 400 mg/m³; 0.2 L @ 2500 mg/m³
-MAX: 20 L @ 400 mg/m³; 3.2 L @ 2500 mg/m³

SHIPMENT: routine

SAMPLE STABILITY: at least 1 week @ 25 °C

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: required; 5 to 10 mL

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD

BIAS: not significant [1]

OVERALL PRECISION (s_r): 0.05 [1]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: naphtha hydrocarbons

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL (packed column);
0.1 to 1 µL (capillary column)

TEMPERATURE-INJECTION: 200 to 250 °C
-DETECTOR: 250 to 300 °C
-COLUMN: 50 to 250 °C @ 8 °/min

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: glass, 3 m x 6 mm, 10% SP-2100 on Supelcoport 80/100 or 30-m fused silica capillary, 0.325-mm ID, 1.0-µm DB-1 or equivalent

CALIBRATION: solutions of bulk naphtha in CS_2

RANGE: 0.5 to 10 mg per sample [2,3,4]

ESTIMATED LOD: 0.1 mg per sample

PRECISION (s_r): 0.01 [1]

APPLICABILITY: The working range is 100 to 2000 mg/m³ for a 5-L air sample. This is a general procedure for analysis of various types of hydrocarbon mixtures called "naphthas" which are used as thinners in paints and varnishes and as general purpose solvents.

INTERFERENCES: Most naphthas are quite complex. The components elute over a wide temperature range by gas chromatography, making interferences from other substances possible. Columns and conditions must be chosen to obtain the desired degree of separation for a given mixture.

OTHER METHODS: This method combines and replaces Methods S86 [2], S380 [3] and S382 [4]. A similar method appears in the criteria document [5].

Preceding page blank

REAGENTS:

1. Eluent: Carbon disulfide*, chromatographic quality, containing 0.1% (v/v) octane, 0.5% (v/v) hexadecane or other suitable internal standard.
   NOTE 1: Use an internal standard which is not a major constituent of the sample.
   NOTE 2: Use toluene in place of carbon disulfide for low-boiling analytes [5].
2. Naphtha bulk sample.
3. Nitrogen or helium, purified.
4. Hydrogen, prepurified.
5. Air, filtered.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1550-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10-µL (1-µL syringe for capillary columns) and other convenient sizes for preparing standards, readable to 0.1 µL
6. Volumetric flasks, 10-mL.
7. Pipet, delivery, 1.0-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size which contains between 0.5 and 8 mg naphtha.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment. Ship a bulk sample (5 to 10 mL) in a separate container from the sorbent tubes.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.1 to 10 mg naphtha per sample.
   a. Add known amounts of naphtha bulk sample to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg naphtha).

9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of naphtha bulk sample directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg naphtha recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1550-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE 1: The columns and conditions given provide moderate to good separation of components. If less resolution is needed, use shorter, less efficient columns as were used in validation of Methods S86 [1], S380 [2] and S382 [3].
    NOTE 2: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of naphtha found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of naphtha in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Methods S86 (Naphtha, Coal Tar), S380 (Petroleum distillate) and S382 (Stoddard Solvent) were issued on March 14, 1975 [2,3,4]. They were validated at 24 °C and approximately 755 mm Hg using 10-, 4- and 3-L air samples, respectively, of 2-50-W Hi-Flash Solvent (Neville Chemical Co.; BP 154 to 195 °C; d 0.893 g/mL), VM&P Naphtha (Amsco Product 1101; BP 120 to 147 °C; d 0.743 g/mL) and Stoddard Solvent (Fisher Scientific Co.; BP 159 to 176 °C; d 0.774 g/mL) [1]. Overall precision and recovery were as shown below, representing a non-significant bias in each method. Breakthrough tests in dry air showed a capacity of 20 to 25 mg of each solvent tested.

Method	Overall Precision (s_r)	Recovery	Range Studied mg/m³	Range Studied mg per sample	Avg. DE	Ref.
S86(b)	0.051	96 ± 7%	193 to 809	2 to 8	0.88	[1,2]
S380(a)	0.052	97 ± 7%	937 to 3930	4 to 16	0.96	[1,3]
S382(b)	0.052	106 ± 7%	1417 to 5940	4.5 to 18	0.95	[1,4]

NOTES: (a) Data based on experiments using an internal standard method with a 10 ft., 1/8" stainless steel column packed with 10% OV-101 on 100/120 mesh Supelcoport.
(b) Data based on experiments using an internal standard method with a 6 ft., 1/8" stainless steel column packed with 1.5% OV-101 on 100/120 mesh Chromosorb W.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S86, S380, S382, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] NIOSH Manual of Analytical Methods, 2nd ed., V. 2, Method S86, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[3] Ibid, V. 3, S380, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[4] Ibid, S382.
[5] Criteria for a Recommended Standard...Occupational Exposure to Refined Petroleum Solvents, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-192 (July, 1977).
[6] NIOSH/OSHA Pocket Guide to Chemical Hazards, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-210 (1978).

METHOD REVISED BY: Ardith A. Grote, NIOSH/DPSE; S86, S380 and S382 originally validated under NIOSH Contract CDC-99-74-55.

Table 1. General information.

Solvent	Boiling Range (°C)	Vapor Pressure, kPa (mm Hg) @ 20 °C	Liquid Density (g/mL @ 15 °C)	Predominant Hydrocarbon Species	Exposure Limits OSHA / NIOSH [5] / ACGIH, mg/m³
Petroleum ether (a)	30 to 60	13 (100) (13 °C)	0.63 to 0.66	C_5-C_6 aliphatic	--- 350 ---
Rubber solvent (a)	45 to 125	(c)	0.67 to 0.85	C_5-C_8 aliphatic	--- 350 1600 (400 ppm)
Petroleum naphtha (b) (Petroleum distillates mixture)	30 to 127	5 (40)	0.6 to 0.8	C_6-C_8	2000 (500 ppm) --- ---
VM&P naphtha (a)	95 to 160	0.3 to 3 (2 to 20)	0.72 to 0.76	C_7-C_{11} < 20% aromatic	--- 350 1350 (300 ppm)
Mineral spirits (a)	150 to 200	0.1 (0.8)	0.77 to 0.81	C_9-C_{12} < 20% aromatic	--- 350 ---
Stoddard solvent (a)	160 to 210	0.5 (4)	0.75 to 0.80	C_9-C_{12} < 20% aromatic	2950 (500 ppm) 350 525 (100 ppm)
Kerosene (a)	175 to 325	(c)	0.8	C_9-C_{16} < 20% aromatic	--- 100 ---
Coal tar naphtha (b)	110 to 190	< 0.7 (<5)	0.86 to 0.89	C_7-C_{10} aromatic	400 (100 ppm) --- ---

(a) As defined by NIOSH Criteria Document [5].
(b) As defined for OSHA PEL [7].
(c) Not available.

FORMULA: NO_2

M.W.: 46.01

NITROGEN DIOXIDE

METHOD: 6700
ISSUED: 2/15/84

OSHA: C 5 ppm
NIOSH: 1 ppm/15 min [1]
ACGIH: 3 ppm; STEL 5 ppm
(1 ppm = 1.881 mg/m³ @ NTP)

PROPERTIES: dark brown fuming liquid or gas; BP 21 °C; MP -11 °C

SYNONYMS: nitrogen peroxide, CAS #10102-44-0.

SAMPLING

SAMPLER: PASSIVE
(Palmes tube with three triethanolamine-treated screens [2])

SAMPLING TIME-MIN: 15 min @ 5 ppm
-MAX: 8 hr @ 10 ppm

SHIPMENT: routine

SAMPLE STABILITY: use sampler within 1 month after preparation; analyze within 1 month after sampling

BLANKS: 5 field blanks per sample set

ACCURACY

RANGE STUDIED: 1.2 to 80 ppm-hrs (0.13 to 8.5 µg NO_2 per sample) [3]

BIAS: complete conversion of nitrogen dioxide to nitrite (Saltzman factor = 1) [2]; slightly lower collection efficiency at lower pressure (-7% at 5,500 m altitude) [4]

OVERALL PRECISION (s_r): 0.06 [5]

MEASUREMENT

TECHNIQUE: VISIBLE ABSORPTION SPECTROPHOTOMETRY

ANALYTE: nitrite ion (NO_2^-)

REAGENT: aqueous solution of sulfanilamide, H_3PO_4 and N-1-naphthylethylene-diamine dihydrochloride

WAVELENGTH: 540 nm

PATHLENGTH: 1 cm

CALIBRATION: solutions of $NaNO_2$ in reagent

RANGE: 0.13 to 8.5 µg NO_2 per sample [3]

ESTIMATED LOD: 0.01 µg NO_2 per sample

PRECISION (s_r): 0.05 [3]

APPLICABILITY: The working range is 1.2 to 80 ppm-hrs [3].

INTERFERENCES: In very dusty environments, particles may deposit on the inside surface of the samplers. Resuspension of the dust in the analytical reagent can give a positive bias in the spectrophotometric reading.

OTHER METHODS: Short-term, long-term, and passive indicator tubes, and various other passive samplers and electrochemical instruments are used. P&CAM 231 [6] and S320 [8] are active solid sorbent sampling methods using similar color development; P&CAM 108 [7] uses a bubbler.

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REAGENTS:

1. Absorbing reagent. 1 volume triethanolamine (TEA) diluted in 7 volumes analytical grade acetone.
2. Sulfanilamide solution. 2 g sulfanilamide + 5 mL conc. H_3PO_4 diluted to 100 mL with distilled H_2O.
3. N-1-naphthylethylenediamine dihydrochloride (NEDA) solution. 70 mg NEDA dissolved in 50 mL distilled H_2O.
4. Combined reagent. 1 volume sulfanilamide solution + 1 volume water + 1/10 volume NEDA solution. Stable ca. one month if protected from light and refrigerated.
5. Sodium nitrite stock solution, 0.05 M. Dissolve 0.345 g (accurately weighed) $NaNO_2$ (reagent grade) in distilled water to make 100 mL solution. Protect from light and keep refrigerated. Stable 90 days.
6. Calibration stock solution. Dilute sodium nitrite stock solution with distilled water. Prepare fresh just before use. For example, a 1:50 dilution yields 1 nanomole NO_2^-/µL.

EQUIPMENT:

1. Sampler: See APPENDIX (potential sources of equipment given in reference [2]):
   a. Acrylic tubing, 3/8 inch (9.5 mm) ID.
   b. Stainless steel screen, 40 x 40 mesh/inch (16 x 16 mesh/cm).
   c. Polyethylene cap, 1/2 inch (12.7 mm, unflanged).
   d. Polyethylene cap, 1/2 inch (12.7 mm, flanged).
   e. Pen clips, 0.48 inch (12.2 mm) I.D.
   f. Electrical tape, plastic.
   g. Stopcock grease.
2. Spectrophotometer, reading at 540 nm, with 1-cm cuvettes.
3. Volumetric flasks and pipets for preparation of standards.
4. Mixer, vibration or vortex (optional).

SPECIAL PRECAUTIONS: None.

SAMPLING:

1. Attach the sampler with flanged cap down. Start sampling by removing flanged cap. Estimate appropriate sampling time such that the amount of NO_2 collected is in the range 1.2 to 80 ppm-hrs (0.13 to 8.5 µg NO_2).
2. Terminate sampling by replacing flanged cap.

CALIBRATION AND QUALITY CONTROL:

3. Calibrate daily.
   a. Prepare a series of working standards just before use over the range 0 to 40 nanomoles (0 to 1.84 µg) NO_2^- per 2.1 mL combined reagent.
   b. Allow 10 min for color development.
   c. Transfer an aliquot of the working standard to a cuvette and analyze (steps 6 through 8).
4. Plot absorbance at 540 nm against NO_2^- mass in nanomoles.
   NOTE: The absorbance of 40 nanomoles NO_2^- is ca. 1 absorbance unit.

5. Check dimensions of the sampler. If cross-sectional area divided by length (A_t/L) of the sampler tube differs significantly from 0.10 cm, recalculate the diffusive collection rate (step 9).

MEASUREMENT:

6. Remove flanged cap from samplers. Add 2.1 mL combined reagent directly into samplers.
   NOTE: If 2.1 mL is not sufficient to completely cover the exit slit of the spectrophotometer, a larger volume can be used provided the same volume is used for both standards and unknowns.
7. Recap the samplers and mix manually or with a mixer. Allow 10 min for the color to develop.
8. Transfer the solution to a cuvette and read the absorbance at 540 nm within 30 min from time reagent was added.
   NOTE: If sample reads beyond calibration graph, dilute sample with combined reagent or extend calibration range.

CALCULATIONS:

9. From calibration graph, read nanomoles NO_2 collected by the sampler. Divide by 2.3 nanomoles/ppm-hr (the diffusive collection rate [2]) and the sample exposure time, t (hr), to obtain time-weighted average concentration, C (ppm NO_2), of NO_2:

$$C = \frac{\text{nanomoles } NO_2}{2.3\ t}$$

   NOTE: Use 2.3•(actual A_t/L [cm] ÷ 0.1 cm) nanomoles/ppm-hr as the diffusive collection rate if sampler dimensions are different from those specified in the APPENDIX.

EVALUATION OF METHOD:

Analytical precision and useful range was estimated from a laboratory evaluation conducted by NIOSH (1982) [3]. Overall precision (s_r = 0.06) was estimated from side-by-side replicate samples collected in a underground salt mine [5]. In a laboratory study, this method gave results averaging 94 ± 4% (mean ± s_r) of a reference method over the range 1.3 to 79 ppm-hrs [3]. A field study found results for this method of 109 ± 9% (mean ± s_r) vs. a reference method in the range 12 to 19 ppm-hrs [5]. Sampling errors may exist in this method when the concentration is not constant in time and the sampling period is short [9,10]. For example, the value of s_r associated with estimating the TWA of an isolated random 10-sec concentration pulse within a 15-min sampling period may be calculated [9] to equal 0.5. Secondly, reference [9] reports a specific set of real-time concentration data measured in an industrial environment. For these data, the error s_r in making 15-min TWA estimates is calculated to equal 0.12. Although these values are large, similar sampling errors due to time variations are expected to be better controlled for longer sampling periods as the variance of the sampling error varies inversely with the sampling period.

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Oxides of Nitrogen (Nitrogen Dioxide and Nitric Oxide), U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-149 (1976).

[2] Palmes, E. D., A. F. Gunnison, J. DeMattio and C. Tomczyk. Personal Sampler for Nitrogen Dioxide, Am. Ind. Hyg. Assoc. J., 37, 570-577 (1976).

[3] Woebkenberg, M. L. A Comparison of Three Personal Passive Sampling Methods for NO_2, Am. Ind. Hyg. Assoc. J., 43, 553-561 (1982).

[4] Lindenboom R. and E. D. Palmes. Effect of Reduced Atmospheric Pressure on a Diffusional Sampler, Am. Ind. Hyg. Assoc. J., 44, 105-108 (1983).
[5] Jones W., E. D. Palmes, C. Tomczyk, and M. Millson. Field Comparison of Two Methods for the Determination of NO_2 Concentration in Air, Am. Ind. Hyg. Assoc. J., 40, 437-438 (1979).
[6] NIOSH Manual of Analytical Methods. 2nd. ed., V. 1, P&CAM 231, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[7] Ibid, P&CAM 108.
[8] Ibid, V. 4, S320, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[9] Bartley, D. L., L. J. Doemeny and D. G. Taylor. Diffusive Monitoring of Fluctuating Concentrations, Am. Ind. Hyg. Assoc. J., 44, 241-247 (1983).
[10] Hearl, F. J. and M. P. Manning. Transient Response of Diffusive Dosimeters, Amer. Ind. Hyg. Assoc. J., 41, 778-783 (1980).

METHOD DEVELOPED BY: E. D. Palmes, New York University [2].

METHOD REVISED BY: William Jones and Frank Hearl, NIOSH/DRDS; Mary Lynn Woebkenberg, NIOSH/DPSE.

APPENDIX:

PREPARATION OF SAMPLER

1. Measure the average cross-sectional area of a length of 3/8 inch (9.5 mm) ID acrylic tubing.
   a. Cap one end of the tubing. Pour in a known volume, v (cm^3), of water to nearly fill the tubing (e.g., 100 mL water for a 180-cm (6-foot) length of tubing).
   b. Measure the height, h (cm), of the water column in the tubing.
   c. Determine the average cross-sectional area, A_t (cm^2), of the tubing.

$$A_t = \frac{v}{h}$$

2. Cut the tubing into lengths, L (ca. 7.1 cm), such that A_t/L = exactly 0.1 cm.
   NOTE: The collection rate is directly proportional to A_t/L. For A_t/L = 0.1 cm, the collection rate is 2.3 nanomoles/ppm-hr [2].
3. Cut circular portions, 13/32 inch (10.3 mm) to 7/16 inch (11.1 mm) in diameter, from stainless steel screen using a 13/32 inch (10.3 mm) paper punch or other suitable means.
4. Clean the tubes, screens and caps with detergent solution in an ultrasonic bath. Rinse with distilled water. Air dry.
5. Dip the screens in absorbing reagent.
6. Using forceps, place the screens on absorbent paper. Press the screens momentarily with the forceps tips to blot. Allow the acetone to evaporate.
7. Stack three treated screens in the bottom of an unflanged cap. Insert the acrylic tube into the unflanged cap securing the screens (see the figures).
8. Slide the pen clip onto the acrylic tube touching the unflanged cap. Secure the pen clip and unflanged cap with a piece of electrical tape.
9. Apply a small amount of stopcock grease to the outside of the uncapped end of the acrylic tube and slide the flanged cap into place.

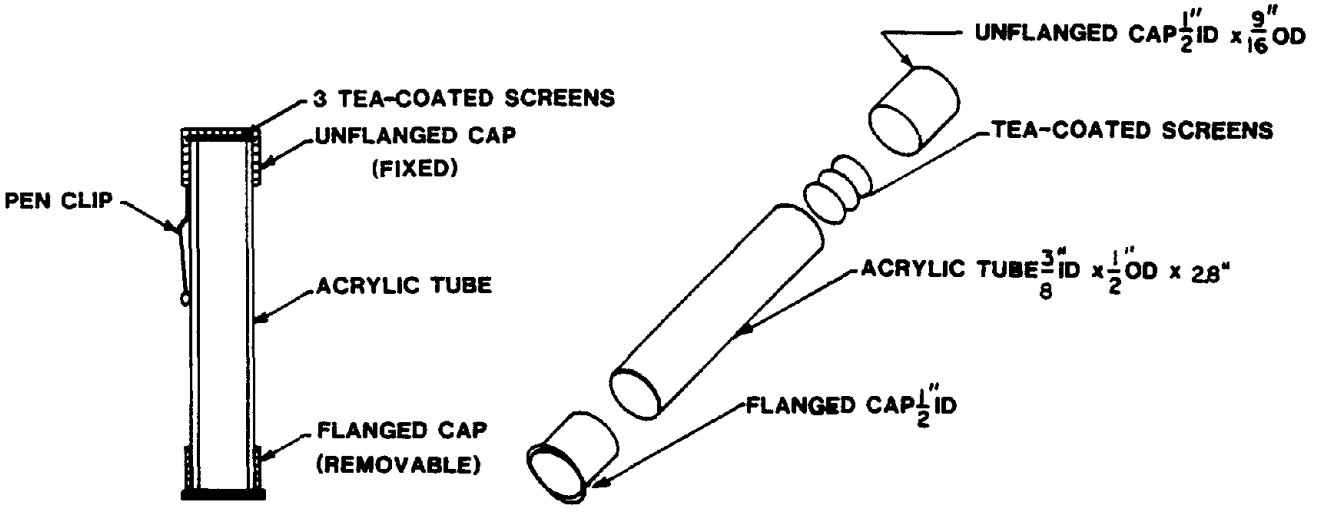

Figure 1. Assembled view (left) and exploded view (right) of sampler.

(1) NITROGLYCERIN, and (2) ETHYL ENE GLYCOL DINITRATE

METHOD: 2507
ISSUED: 2/15/84

FORMULA: (1) $(CH_2ONO_2)_2CH(ONO_2)$; $C_3H_5N_3O_9$
(2) $O_2NOCH_2CH_2ONO_2$; $C_2H_4N_2O_6$

M.W.: (1) 227.09; (2) 152.06

OSHA: (1 and 2) C 0.2 ppm (skin)
NIOSH: (1 and 2) 0.1 mg/m³/20 min [1]
ACGIH: (1 and 2) 0.05 ppm (skin)
[1 ppm @ NTP = 9.28 mg/m³ (1); 6.22 mg/m³ (2)]

PROPERTIES: (1) liquid; MP 3 to 13 °C; d 1.592 g/mL @ 25 °C; VP 0.034 Pa (0.00026 mm Hg; 0.34 ppm) @ 20 °C;
(2) liquid; MP -22 °C; explodes @ 114 °C; d 1.49 g/mL @ 25 °C; VP 6.8 Pa (0.05 mm Hg; 68 ppm) @ 20 °C

SYNONYMS: (1) nitroglycerin: NG; 1,2,3-propanetriol trinitrate; CAS #55-63-0.
(2) ethylene glycol dinitrate: EGDN; ethylene dinitrate; CAS #628-96-6.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(Tenax-GC, 100 mg/50 mg)

FLOW RATE: 0.2 to 1.0 L/min

VOL-MIN: 3 L @ 1 mg/m³ (1) or (2)
-MAX: 100 L

SHIPMENT: routine

SAMPLE STABILITY: at least 25 days @ 25 °C [5]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: (1) 0.6 to 3.2 mg/m³ [2,3];
(2) 0.5 to 1.8 mg/m³ [1,3]

BIAS: not significant [3]

OVERALL PRECISION (s_r): (1) 0.104 [2];
(2) 0.089 [2]

MEASUREMENT

!
!TECHNIQUE: GAS CHROMATOGRAPHY, ECD
!
!ANALYTE: NG and EGDN
!
!DESORPTION: 2 mL ethanol; stand 30 min
!
!INJECTION VOLUME: 2 µL
!
!TEMPERATURE-INJECTION: 160 °C (DNE 160 °C)
! -DETECTOR: 280 °C
! -COLUMN: 125 °C (DNE 150 °C)
!
!CARRIER GAS: 95% argon/methane , 75 mL/min
!
!COLUMN: glass, 1 m x 4 mm, 2 mm ID 10% OV-17 on
! 60/80 mesh Gas Chrom Q
!
!CALIBRATION: solutions of analytes in ethanol
!
!RANGE: 3 to 45 µg per sample
!
!ESTIMATED LOD: 0.6 µg per sample
!
!PRECISION (s_r): (1) 0.051 [2];
! (2) 0.063 [2]
!

APPLICABILITY: The working range for both compounds is 0.2 to 3 mg/m³ for a 15-L air sample, provided that the linear range of the ECD is not exceeded.

INTERFERENCES: A high concentration of 2-hydroxyethyl nitrate (ethylene glycol mononitrate) tails into the EGDN peak but does not prevent a satisfactory determination of EGDN.

OTHER METHODS: This method combines and replaces Methods S216 [1,2] and P&CAM 203 [4].

Preceding page blank

REAGENTS:

1. Ethanol, absolute.*
2. Nitroglycerin (NG)* - one of the following:
   a. pure material.
   b. standard solution in ethanol, available from dynamite manufacturer.
   c. tablets, sublingual, USP (analyzed; 80 to 112% NG).
      NOTE: to prepare solutions, weigh, crush and extract with ethanol. Filter and dilute to volume.
   d. nitroglycerin lactose trituration, available from NG tablet manufacturer.
3. Ethylene glycol dinitrate (EGDN)* - one of the following:
   a. pure material.
   b. dynamite, analyzed, available
   NOTE: Dynamite is heterogenerous. Use care to obtain representative sample.
4. Argon/methane, 95:5 (v/v), purified.
6. Calibration stock solution, 0.3 µg/µL. Dilute 1 mL DE stock solution to 10 mL with ethanol.
5. DE stock solution, 3 µg/µL. Dissolve 30.0 mg NG and/or 30.0 mg EGDN in ethanol to make 10 mL solution.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 10 cm long, 8 mm OD, flame-sealed ends and plastic caps, containing two sections of 35/60 mesh Tenax-GC resin (front = 100 mg; back = 50 mg), separated by a urethane foam plug. Silylated glass wool plugs precede the front section and follow the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.2 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, ECD, integrator and column (page 2507-1).
4. Vials, 5-mL, with PTFE-lined caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Pipets, 2-mL, delivery, glass, with pipet bulb.
7. Volumetric flasks, 1- and 10-mL.

SPECIAL PRECAUTIONS: Ethanol is flammable and all work should be done in an exhaust hood and away from any open flame.

Nitroglycerin and ethylene glycol dinitrate can be explosive in their pure forms and extreme caution should be used when handling the bulk material [1].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.2 and 1 L/min for a total sample size of 3 to 100 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 2.0 mL ethanol to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 1 to 45 µg NG or EGDN per sample.
   a. Add known amounts of calibration stock solution to ethanol in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. µg NG or EGDN).
9. Determine desorption efficiency (DE) at least once for each batch of Tenax-GC used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of DE stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. µg NG or EGDN recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2507-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with ethanol, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE) of NG or EGDN found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of NG or EGDN in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S216 [3] was issued on November 11, 1975, and validated over the range of 0.56 to 3.2 mg/m³ for nitroglycerin and 0.51 to 1.8 mg/m³ for ethylene glycol dinitrate [2]. Eighteen 15-L samples for each analyte were taken of dynamically-generated test atmospheres. Eighteen additional samples for each analyte were spiked (six each at one-half, one and two times the OSHA standard) directly. The average recovery for all three levels for nitroglycerin was 97.6% and had a pooled precision (s_r) of 0.051. The average recovery for the three

levels for ethylene glycol dinitrate was 92.0% with a pooled precision (s_p) of 0.063. Since the collection efficiency of the Tenax-GC for both compounds was established as 100%, the corrected "found" value of the generated sample was taken as the measure of the generated air concentrations. Breakthrough for each compound was evaluated at a concentration twice the OSHA standard. Duplicate samples were collected at interim periods of 60, 120, and 240 min at 1.1 L/min. Breakthrough of EGDN occurred at some point between 130 and 257 L of air sampled. No breakthrough occurred with the NG samples up to an average sample volume of 261 L. Sample stability was evaluated with 2.6 µg EGDN per sample and 9.0 µg NG per sample for 25 days at ambient temperature. No losses were observed for either compound [5].

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Nitroglycerin and Ethylene Glycol Dinitrate, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-167 (1978).

[2] Documentation of the NIOSH Validation Tests, S216, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).

[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3, S216, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

[4] Ibid, V. 1, P&CAM 203, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).

[5] Sampling and Analysis of Four Organic Compounds Using Solid Sorbents, Final Report, NIOSH Contract No. HSM-99-73-63, Southern Research Institute, Birmingham, AL.

METHOD REVISED BY: Martha J. Seymour, NIOSH/DPSE; S216 validated under NIOSH Contract CDC-99-74-45.

FORMULA: N≡N=O; N_2O

M.W.: 44.01

NITROUS OXIDE

METHOD: 6600
ISSUED: 2/15/84

OSHA: no standard
NIOSH: 25 ppm if used with other anesthetics;
50 ppm if sole anesthetic [1]
ACGIH: no standard
(1 ppm = 1.80 mg/m³ @ NTP)

PROPERTIES: gas; BP -88.46 °C; d = 1.53 (air = 1)

SYNONYMS: laughing gas; hyponitrous acid anhydride; CAS #10024-97-2.

SAMPLING

SAMPLER: AMBIENT AIR OR BAG SAMPLE

VOL-MIN: at least 2 spectrophotometer cell volumes
-MAX: no maximum volume

SAMPLE STABILITY: bag samples stable 2 hrs @ 25 °C

BLANKS: use uncontaminated air

ACCURACY

RANGE STUDIED: 10 to 1000 ppm

BIAS: none known

OVERALL PRECISION (s_r): 0.013 [2]
(between-instrument)

MEASUREMENT

!
!TECHNIQUE: LONG-PATHLENGTH PORTABLE INFRARED
! SPECTROPHOTOMETER (FIELD READOUT)
!
!ANALYTE: nitrous oxide
!
!OPERATION: according to manufacturer's
! instructions
!
!ANALYTICAL WAVELENGTH: 4.48 µm
!
!PATHLENGTH: 0.5 m to 40 m (function of desired
! concentration range)
!
!CALIBRATION: closed-loop dilution of N_2O
!
!RANGE: 10 ppm to > 1% N_2O in air
!
!ESTIMATED LOD: ca. 1 ppm N_2O @ 10 m
! pathlength; varies with pressure
! and instrument
!
!PRECISION (s_r): 0.01 [2]
!(within-instrument)
!

APPLICABILITY: The working range of this method is 10 ppm (v/v) to more than 1% (v/v) N_2O. This method may be used for the sequential determination of two or more analytes by changing the analytical wavelength and pathlength.

INTERFERENCES: In common application (i.e., hospital, dental or veterinary operatory), there are no identified interferences.

OTHER METHODS: The criteria document on waste anesthetic gases [1] also describes an infrared method.

REAGENTS:

1. Nitrous oxide, 99%, compressed.*
   NOTE: Required in field for calibration.
2. Air, uncontaminated.

*See Special Precautions.

EQUIPMENT:

1. Spectrophotometer: infrared analyzer, transportable, long pathlength (0.5 to 40 m, as needed for concentration range measured), wavelength 4.48 μm, sample cell of known volume.
   NOTE: Readout drift should be less than 5% full-scale/8-hr.
2. Pump to circulate air samples through the spectrophotometer sample cell; flow rate ca. 1 sample cell volume/min.
3. Syringes, gas-tight, 0.1-, 0.5- and 1-mL.
4. Regulator for nitrous oxide.
5. Strip chart recorder, compatible with spectrophotometer (optional).
6. Personal sampling pump, 0.1 to 4 L/min, capable of bag filling, with flexible connecting tubing; and plastic bags, inert and impermeable, clean, various sizes, capacity $\geq$ 2 times spectrophotometer cell volume (optional; for TWA samples).
7. Plastic tubing (optional; for remote, real-time analysis).

SPECIAL PRECAUTIONS: Nitrous oxide supports combustion. Shipment of compressed calibration gas must comply with 49 CFR 171-177 regulations regarding shipment of hazardous materials.

SAMPLING:

1. Select one of the following sampling modes according to the desired form of the data:
   a. Ambient air. Pump ambient air at ca. 1 cell volume/min through the spectrophotometer sample cell.
      NOTE 1: Record and integrate the continuous spectrophotometer output signal if data are to be expressed as TWA concentration.
      NOTE 2: Remote air samples may be transported to the spectrophotometer with the use of plastic tubing and a vacuum pump and analyzed in the same manner as ambient air samples.
   b. Integrated air samples for TWA determinations.
      (1) Evacuate a clean plastic bag.
      (2) Attach the plastic bag to a personal sampling pump and pump the air to be sampled into the bag at a rate calculated to fill the bag over the duration of the sampling period. Terminate sampling before the bag is 80% full.
      NOTE: The flow rate must remain within $\pm$ 5% of the initial setting throughout the sampling period.
      (3) Analyze the bag sample within 2 hrs after completion of sampling to minimize loss of analyte by adsorption and permeation.

INSTRUMENT PREPARATION AND CALIBRATION:

2. Set instrument parameters as required for analysis. Allow sufficient warm-up/equilibration time.

3. Perform on-site multi-point calibration at five or more concentrations over the range 10 to 1000 ppm.
   a. Zero instrument while recirculating uncontaminated air through sample cell.
   b. Inject known volume of N_2O into the sample cell with a gas-tight syringe.
      NOTE: Inject the N_2O through tubing or a septum attached to the sample cell.
   c. Calculate concentration, C_S (ppm), of N_2O in sample cell:

$$C_S = \frac{\text{Volume of } N_2O \text{ injected } (\mu L)}{\text{Volume of cell } (L)}, \text{ ppm.}$$

   d. When instrument reading stabilizes, record meter or recorder deflection.
   e. Prepare calibration graph (C_S vs. meter or recorder deflection).
4. Practice routine instrument maintenance.
   a. Replace septa in a closed-loop system frequently in accordance with manufacturer's recommendations.
   b. Check and replace, if cloudy, the NaCl windows in the infrared spectrophotometer.
      NOTE: AgBr optics cloud less quickly.
   c. Follow manufacturer's recommendations for specific routine maintenance.

MEASUREMENT:

5. Pump air to be analyzed through sample cell to purge the sample cell. Typically, 2 to 3 cell volumes are necessary. When output stabilizes, record meter or recorder reading.
6. Read the concentration of N_2O in the unknown samples, C_V (ppm), corresponding to the meter or recorder deflection directly from the calibration graph.
7. Periodically during each day's operation recheck calibration by going to step 2 and repeating three or more points on the calibration graph.

EVALUATION OF METHOD:

This method has been successfully used in hospital, dental and veterinary operatories. Calibration curves have proven reproducible. Individual data sets have demonstrated statistical comparability in Bartlett's test for homogeneity. Relative standard deviations, s_r, as low as 0.006 have been seen in replicate calibrations of the same instrument by different individuals in the 10 to 1000 ppm range [2].

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Waste Anesthetic Gases and Vapors, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-140 (1977).
[2] Burroughs, G. E. NIOSH, Division of Physical Sciences and Engineering, unpublished data (1983).

METHOD WRITTEN BY: G. E. Burroughs and M. L. Woebkenberg, NIOSH/DPSE.

DEFINITION: Total aerosol mass

NUISANCE DUST, TOTAL

METHOD: 0500
ISSUED: 2/15/84

OSHA: 15 mg/m³
NIOSH: no standard
ACGIH: 10 mg/m³, total dust less than 1% quartz

PROPERTIES: quartz less than 1% [1]

SYNONYMS: boron oxide (CAS #1303-86-2) and nuisance dusts [1] including alumina (CAS #1344-28-1), calcium carbonate (CAS #1317-65-3), cellulose (paper fiber; CAS #9004-34-6), glycerin mist (CAS #56-81-5), limestone (CAS #1317-65-3), etc.

SAMPLING

SAMPLER: FILTER
(tared 37-mm, 5-µm PVC filter)

FLOW RATE: 1.5 to 2 L/min

VOL-MIN: 25 L @ 15 mg/m³
-MAX: 133 L @ 15 mg/m³

SHIPMENT: routine

SAMPLE STABILITY: indefinitely

BLANKS: 2 field blanks per 10 samples

BULK SAMPLE: none required

ACCURACY

RANGE STUDIED: 8 to 28 mg/m³

BIAS: not significant

OVERALL PRECISION (s_r): 0.056 [2]

MEASUREMENT

TECHNIQUE: GRAVIMETRIC (FILTER WEIGHT)

ANALYTE: airborne particulate material

BALANCE: 0.01 mg sensitivity or better; use same balance before and after sample collection

CALIBRATION: National Bureau of Standards Class M weights

RANGE: 0.3 to 2 mg per sample

ESTIMATED LOD: 0.2 mg per sample

PRECISION: 0.08 mg per sample [3]

APPLICABILITY: The working range is 3 to 20 mg/m³ for a 100-L air sample. This method is nonspecific and determines the total dust concentration to which a worker is exposed. It may be applied, e.g., to gravimetric determination of fibrous glass [4] in addition to the other ACGIH nuisance dusts [1].

INTERFERENCES: Organic and volatile particulate matter may be removed by dry ashing [4].

OTHER METHODS: This method is similar to the criteria document method for fibrous glass [4] and Method 5000 for carbon black. This method replaces Method S349 [5]. Impingers and direct-reading instruments may be used to collect total dust samples, but these have limitations for personal sampling.

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EQUIPMENT:

1. Environmental chamber at constant temperature and humidity (e.g., 20 °C ± 0.3 °C and 50% ± 5% RH).
2. Sampler: 37-mm PVC, 2- to 5-μm pore size membrane or equivalent hydrophobic filter and cellulose supporting pad in 37-mm cassette filter holder.
3. Personal sampling pump, 1.5 to 2 L/min, with flexible connecting tubing.
4. Microbalance, capable of weighing to 0.01 mg.
5. Vacuum desiccator.
6. Static neutralizer: e.g., Po-210; replace nine months after the production date.

SPECIAL PRECAUTIONS: None.

PREPARATION OF FILTERS BEFORE SAMPLING:

1. Dry filters and backup pads under vacuum in the vacuum desiccator for at least 15 min.
2. Release the vacuum, remove the desiccator cover and equilibrate the filters in the environmental chamber for at least 1 hr.
3. Number the backup pads with a ballpoint pen and place them, numbered side down, in filter cassette bottom sections.
4. Weigh the filters in the environmental chamber. Record the filter tare weight, W_1 (mg).
   a. Zero the balance before each weighing.
   b. Handle the filter with forceps (nylon forceps if further analyses will be done).
   c. Pass the filter over an antistatic radiation source. Repeat this step if filter does not release easily from the forceps or if filter attracts balance pan. Static electricity can cause erroneous weight readings.
5. Place the weighed filters on top of the backup pads in the filter cassette bottom sections and allow to stand an additional 8 to 16 hrs in the environmental chamber.
6. Reweigh the filters. If this tare weight differs by more than 0.01 mg from the first tare weight obtained in step 4 above, discard the filter.
   NOTE: Insert a rod through the outlet hole of the filter cassette bottom section to raise the backup pad and filter so that the filter can be grasped with forceps.
7. Assemble the filter in the filter cassettes and close firmly so that leakage around the filter will not occur. Place a plug in each opening of the filter cassette. Place a cellulose shrink band around the filter cassette, allow to dry and mark with the same number as the backup pad.

SAMPLING:

8. Calibrate each personal sampling pump with a representative sampler in line.
9. Sample at 1.5 to 2 L/min. Do not exceed a total filter loading of approximately 2 mg total dust.

SAMPLE PREPARATION:

10. Wipe dust from the external surface of the filter cassette with a moist paper towel to minimize contamination. Discard the paper towel.
11. Remove the top and bottom plugs from the filter cassette. Place the filter cassettes in a vacuum desiccator under vacuum for at least 15 min, followed by equilibration for at least 1 hr in the environmental chamber.
12. Remove the cassette band, pry open the cassette and remove the filter. Handle the filters very gently by the edge to avoid loss of dust.

NOTE: If the filter sticks to the underside of the cassette top, very gently lift away by using the dull side of a scalpel blade. This must be done carefully or the filter will tear.

CALIBRATION AND QUALITY CONTROL:

13. Zero the microbalance before all weighings. Use the same microbalance for weighing filters before and after sample collection. Maintain and calibrate the balance with National Bureau of Standards Class M weights.
14. Take two to four replicate samples for every batch of field samples for quality assurance on the sampling procedures. The set of replicate samples should be exposed to the same dust environment, either in a laboratory dust chamber [6] or in the field. The quality control samples must be taken with the same equipment, procedures and personnel used in the routine field samples. The relative standard deviation calculated from these replicates should be recorded on control charts and action taken when the precision is out of control.

MEASUREMENT:

15. Weigh each filter, including field blanks. Record this post-sampling weight, W_2 (mg), beside its corresponding tare weight. Record anything remarkable about a filter (e.g., overload, leakage, wet, torn, etc.).

CALCULATIONS:

16. Calculate the concentration of total nuisance dust, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{(W_2 - W_1) + B}{V} \cdot 10^3, \ mg/m^3$$

where: W_1 = tare weight of filter before sampling (mg)
W_2 = post-sampling weight of sample-containing filter (mg)
B = mean change in field blank filter weights between tare and post-sampling (mg) (+ or -).

EVALUATION OF METHOD:

Lab testing with blank filters and generated atmospheres of carbon black was done at 8 to 28 mg/m^3 [2,6]. Precision and accuracy data are given on page 0500-1.

REFERENCES:

[1] TLVs - Threshold Limit Values for 1983-84, Appendix D, ACGIH, Cincinnati, OH (1983).
[2] This Manual, Method 5000.
[3] Unpublished data from Non-textile Cotton Study, NIOSH/DRDS/EIB.
[4] NIOSH Criteria for a Recommended Standard ... Occupational Exposure to Fibrous Glass, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-152, 119-142 (1977).
[5] NIOSH Manual of Analytical Methods, 2nd ed., V. 3, S349, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[6] Documentation of the NIOSH Validation Tests, S262 and S349, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).

METHOD WRITTEN BY: Kathy Morring, Jerry Clere, and Frank Hearl, P.E., NIOSH/DRDS.

NUISANCE DUST, RESPIRABLE

METHOD: 0600
ISSUED: 2/15/84

FORMULA: The respirable fraction of the dust mass, as specified by the American Conference of Governmental Industrial Hygienists [1]

OSHA: 5 mg/m³
NIOSH: no standard
ACGIH: 5 mg/m³

PROPERTIES: Penetrates the non-ciliated portions of the lung; quartz less than 1%

SYNONYMS: boron oxide (CAS #1303-86-2) and nuisance dusts [2], including alumina (CAS #1344-28-1), calcium carbonate (CAS #1317-65-3), cellulose (paper fiber; CAS #9004-34-6), glycerin mist (CAS #56-81-5), limestone (CAS #1317-65-3), etc.

SAMPLING

SAMPLER: CYCLONE + FILTER (10-mm Dorr-Oliver cyclone + tared 5-µm PVC membrane)

FLOW RATE: 1.7 L/min

VOL-MIN: 75 L @ 5 mg/m³
-MAX: 1000 L @ 5 mg/m³

SHIPMENT: routine

SAMPLE STABILITY: indefinitely

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.5 to 10 mg/m³ (lab and field)

BIAS: depends on dust size distributions [3]

OVERALL PRECISION (s_r): 0.043 to 0.145 (lab); 0.144 to 0.227 (field) [4]

MEASUREMENT

TECHNIQUE: GRAVIMETRIC (FILTER WEIGHING)

ANALYTE: mass of respirable dust fraction

BALANCE: 0.01 mg sensitivity or better; use same balance before and after sample collection

CALIBRATION: National Bureau of Standards Class M weights

RANGE: 0.3 to 2 mg per sample

ESTIMATED LOD: 0.2 mg per sample

PRECISION: 68 µg with 0.01-mg sensitivity balance [5]

APPLICABILITY: The method measures the mass concentration of any non-volatile respirable dust. Besides inert dusts [1], the method is recommended for respirable coal dust, which has an OSHA PEL = 2.4 mg/m³. The method may be biased where the respirable fraction is defined by the British Medical Research Council's criteria or the MRE horizontal elutriator [4].

INTERFERENCES: Larger than respirable particles (over 10 µm) have been found in some cases by microscopic analysis of cyclone filters. Over-sized particles in the sample are known to be caused by inverting the cyclone assembly. Heavy dust loadings, charged particles, fibers and water-saturated dusts also interfere with the cyclone's size-selective properties.

OTHER METHODS: This method is based on and replaces Sampling Data Sheet #29.02 [6].

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EQUIPMENT:

1. Sampler:
   a. Filter: 37-mm diameter, 5.0-μm pore size, polyvinyl chloride filter or equivalent hydrophobic membrane filter supported with backup pad in a two-piece, 37-mm cassette filter holder held together by tape or cellulose shrink band.
   b. Cyclone: 10-mm Dorr-Oliver nylon cyclone.
   c. Sampling head holder: this holder must keep the cassette, cyclone and coupler together rigidly so that air enters only at the cyclone inlet.
2. Personal sampling pump, 1.7 L/min ± 5%, with flexible connecting tubing.
   NOTE: Pulsation in the pump flow must be within ± 20% of the mean flow.
3. Balance, analytical, with sensitivity of at least 0.01 mg. A more sensitive balance will be necessary for substances with PEL's below 1 mg/m^3.
4. Static neutralizer, e.g., Po-210; replace nine months after the production date.
5. Environmental chamber for balance, e.g., 20 °C ± 0.3 °C and 50% ± 5% RH.
6. Vacuum desiccator.

SPECIAL PRECAUTIONS: None.

PREPARATION OF SAMPLERS BEFORE SAMPLING:

1. Dry filters and backup pads under vacuum in the vacuum desiccator for at least 15 min.
2. Release the vacuum, remove the desiccator cover, and equilibrate the filters in the environmental chamber for at least 1 hr.
3. Number the backup pads with a ballpoint pen and place them, numbered side down, in filter cassette bottom sections.
4. Weigh the filters in the environmental chamber. Record the filter tare weight, W_1 (mg).
   a. Zero the balance before each weighing;
   b. Handle the filter with forceps (nylon forceps if further analyses will be done); and
   c. Pass the filter over an antistatic radiation source. Repeat this step if filter does not release easily from the forceps or if filter attracts balance pan. Static electricity can cause erroneous weight readings.
5. Place the weighed filters on top of the backup pads in the filter cassette bottom sections and allow to stand an additional 8 to 16 hrs in the environmental chamber.
6. Reweigh the filters. If this tare weight differs by more than 0.01 mg from the first tare weight obtained in step 4 above, discard the filter.
   NOTE: Insert a rod through the outlet hole of the filter cassette bottom section to raise the backup pad and filter so that the filter can be grasped with forceps.
7. Assemble the filters in the filter cassettes and close firmly so that leakage around the filter will not occur. Place a plug in each opening of the filter cassette. Place a cellulose shrink band around the filter cassette, allow to dry, and mark with the same number as the backup pad.
8. Remove the cyclone's grit cap and vortex finder before use and inspect the cyclone interior. If the inside is visibly scored, discard this cyclone since the dust separation characteristics of the cyclone might be altered. Clean the interior of the cyclone to prevent reentrainment of large particles.
9. Assemble the sampler head. Check alignment of filter holder and cyclone in the sampling head to prevent leakage.

SAMPLING:

10. Calibrate each personal sampling pump to 1.7 L/min with a representative sampler in line.
11. Sample at 1.7 L/min for 45 min to 8 hrs (76 to 816 L). Do not exceed 5 mg dust loading on the filter.
    NOTE: Do not allow the sampler assembly to be inverted at any time. Turning the cyclone to anything more than a horizontal orientation may deposit over-sized material from the cyclone body onto the filter.

SAMPLE PREPARATION:

12. Wipe dust from the external surface of the filter cassette with a moist paper towel to minimize contamination. Discard the paper towel.
13. Remove the top and bottom plugs from the filter cassette. Place the filter cassettes in a vacuum desiccator under vacuum for at least 15 min, followed by equilibration for at least 1 hr in the environmental chamber.
14. Remove the filter cassette band, pry open the filter cassette, and remove the filter by inserting a rod in the outlet hole of the filter cassette. Handle the filters very gently by the edge to avoid loss of dust.
    NOTE: If the filter sticks to the underside of the cassette top, very gently lift away by using the dull side of a scalpel blade. This must be done carefully or the filter will tear.

CALIBRATION AND QUALITY CONTROL:

15. Zero the microbalance before all weighings. Use the same microbalance for weighing filters before and after sample collection. Calibrate the balance with National Bureau of Standards Class M weights.
16. Take two to four replicate samples for every batch of field samples for quality assurance on the sampling procedures. The set of replicate samples should be exposed to the same dust environment, either in a laboratory dust chamber [7] or in the field [8]. The quality control samples must be taken with the same equipment, procedures and personnel used in the routine field samples. Calculate precision from these replicates and record s_r on control charts. Take corrective action when the precision is out of control [7].

MEASUREMENT:

17. Weigh each filter, including field blanks. Record this post-sampling weight, W_2 (mg), beside its corresponding tare weight. Record anything remarkable about a filter (e.g., visible particles, overloaded, leakage, wet, torn, etc.).

CALCULATIONS:

18. Calculate the concentration of respirable nuisance dust, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{(W_2 - W_1) + B}{V} \cdot 10^3, \ mg/m^3$$

where: W_1 = tare weight of filter before sampling (mg)
W_2 = post-sampling weight of sample-containing filter (mg)
B = mean change in field blank filter weights between tare and post-sampling (mg) (+ or -).

EVALUATION OF METHOD:

1. Bias. In respirable dust measurements, the bias in a sample is calculated relative to the appropriate respirable dust criterion. The theory for calculating bias is developed by Bartley and Breuer [3]. For this method, the bias, therefore, depends on the ACGIH criterion for respirable dust, the cyclone's penetration curve at 1.7 L/min flow rate, and the size distribution of the ambient dust. Based on the cyclone's penetration curves for non-pulsating flow measured with a monodisperse aerosol by Caplan, Doemeny and Sorenson [9], the bias in this method is shown in Figure 1.

   For dust size distributions in the shaded region, the bias in this method lies within the $\pm$ 0.10 criterion established by NIOSH for method validation. Bias larger than $\pm$ 0.10 would, therefore, be expected for many workplace aerosols, especially those with small mass median diameters. However, bias within $\pm$ 0.20 would be expected for dusts with geometric standard deviations greater than 2.0, which is the case in most workplaces.

   Bias can also be caused in a cyclone by the pulsation of the personal sampling pump. Bartley, et al. [10] showed that cyclone samples with pulsating flow can have negative bias as large as -0.22 relative to samples with steady flow. The magnitude of the bias depends on the amplitude of the pulsation at the cyclone aperture and the dust size distribution. For pumps with instantaneous flow rates within 20% of the mean, the pulsation bias is less than -0.02 for most dust size distributions encountered in the workplace.

   Electric charges on the dust and the cyclone will also cause bias. Briant and Moss [11] have found electrostatic biases as large as -50%, and show that cyclones made with graphite-filled nylon eliminate the problem.

2. Precision. In a recent review [4], the overall cyclone precision is shown to be most sensitive to two factors: the analytical precision and the sampling procedures, particularly the quality control system used in the maintenance and calibration of samplers. Theoretically, the variance for the overall precision is the sum of the variances from the sampling and analysis. The analytical variance depends on the dust loading on the filter. For the dust loading in an 8-hr sample above 1.5 mg/m^3, Bowman, et al. [4] find that the empirically determined sampling error dominates this analytical error.

   Because of the effects of the environment, precision estimates for dust samplers are much more variable than those reported for gas and vapor sampling. In laboratory tests with 0.01 mg sensitivity balances, the overall precision of a single respirable dust sample has relative standard deviations (s_r) from 0.043 to 0.145 over concentrations ranging from 0.5 to 5 mg/m^3. In the laboratory studies where the dust concentrations in the test chamber are more carefully controlled, the estimated s_r is less than 0.091, which is the target precision value for a bias equal to $\pm$ 0.10 in the NIOSH validation criteria.

   In the field tests with 0.01 mg sensitivity balances, precision estimates range from 0.144 to 0.227 over concentrations ranging from 1 to 10 mg/m^3. Whether the larger s_r values in field tests are due to sampler performance or to more inhomogeneous dust concentrations in the field tests cannot be determined from existing data.

REFERENCES:
[1] TLVs - Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment with Intended Changes for 1983-84, 38, ACGIH, Cincinnati, OH (1983).
[2] Ibid, Appendix D, 52.
[3] Bartley, D. L. and G. M. Breuer. Analysis and Optimization of the Performance of the 10-mm Cyclone, Am. Ind. Hyg. Assoc. J., 43, 520-528 (1982).
[4] Bowman, J. D., D. L. Bartley, G. M. Breuer and S. A. Shulman. The Accuracy of Sampling Respirable Coal Mine Dust, Draft NIOSH report (1983).
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[6] NIOSH Manual of Sampling Data Sheets, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-159 (1977).
[7] Bowman, J. D., D. L. Bartley, G. M. Breuer, L. J. Doemeny and D. J. Murdock. Accuracy Criteria Recommended for the Certification of Gravimetric Coal Mine Dust Personal Samplers, NIOSH report (in press, 1983).
[8] Breslin, J. A., S. J. Page and R. A. Jankowski. Precision of Personal Sampling of Respirable Dust in Coal Mines, U.S. Bureau of Mines Report of Investigations #8740 (1983).
[9] Caplan, K. J., L. J. Doemeny and S. Sorenson. Evaluation of Coal Mine Dust Personal Sampler Performance, Final Report, NIOSH Contract No. PH CPE-r-70-0036 (1973).
[10] Bartley, D. L., G. M. Breuer, P. A. Baron and J. D. Bowman. Pump Fluctuations and Their Effect on Cyclone Performance, submitted to the Am. Ind. Hyg. Assoc. J. (1983).
[11] Briant, J. K. and O. R. Moss. The Influence of Electrostatic Charge on the Performance of 10-mm Nylon Cyclones, American Industrial Hygiene Conference (1983).

METHOD WRITTEN BY: Joseph Bowman, Ph.D., CIH, NIOSH/DPSE.

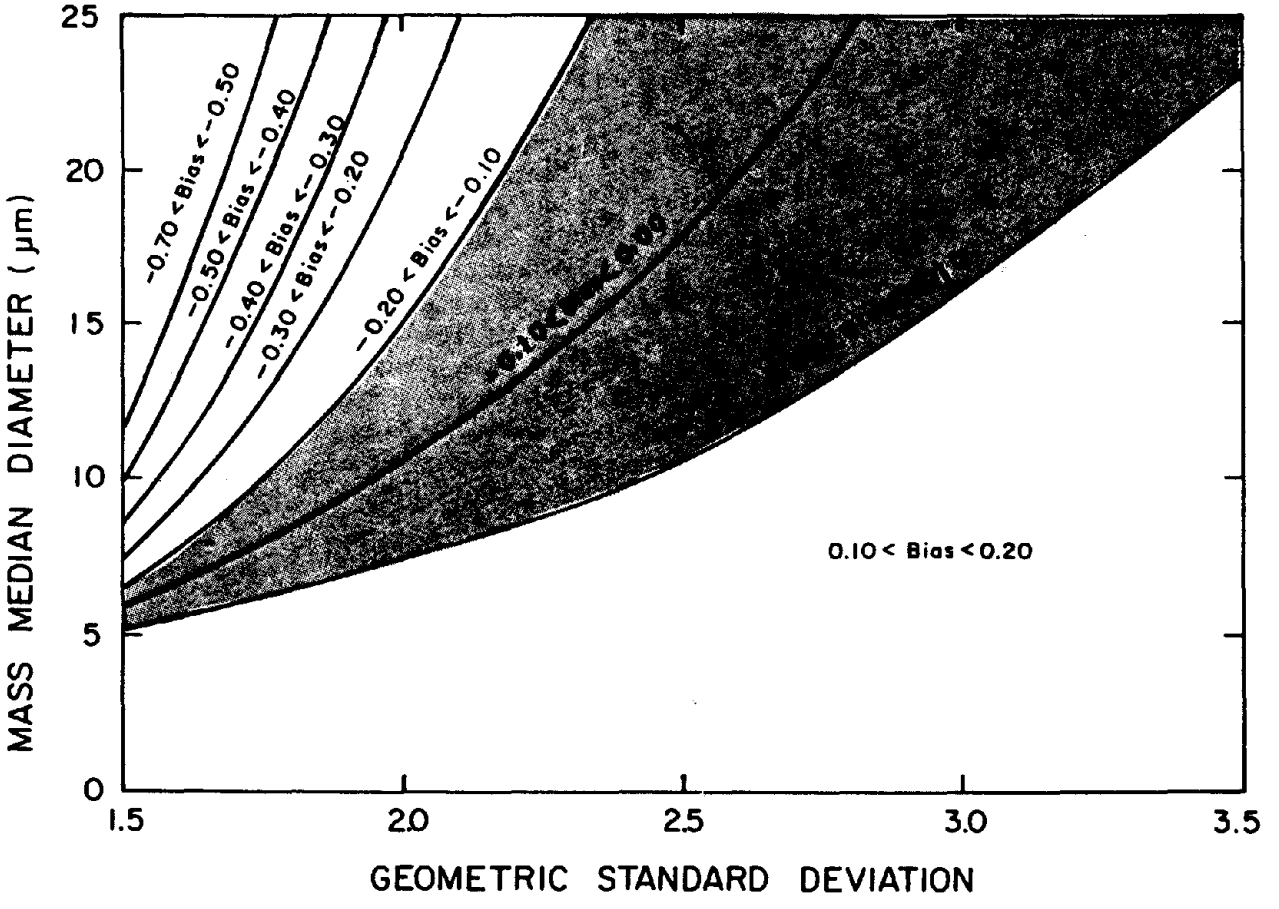

Figure 1. Bias in respirable dust determination.

FORMULA: $CH_3(CH_2)_7SH$; $C_8H_{18}S$

M.W.: 146.30

1-OCTANETHIOL

METHOD: 2510
ISSUED: 2/15/84

OSHA: no standard
NIOSH: 3.0 mg/m³/15 min [1]
ACGIH: no standard
(1 ppm = 5.98 mg/m³ @ NTP)

PROPERTIES [3]: liquid; d 0.843 g/mL @ 20 °C; BP 199.1 °C; MP -49.2 °C

SYNONYMS: n-octanethiol; octylmercaptan; 1-mercaptooctane; octyl thiol; CAS #111-88-6.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(Tenax-GC, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 1 L @ 3 mg/m³ (0.5 ppm)
-MAX: 15 L

SHIPMENT: routine

SAMPLE STABILITY: at least 8 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.32 to 6.55 mg/m³ [2]
(8.5-L samples)

BIAS: -0.013 [2]

OVERALL PRECISION (s_r): 0.083 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, SULFUR-SPECIFIC FPD

ANALYTE: 1-octanethiol (sulfur)

DESORPTION: 2 mL acetone; 30 min ultrasonic agitation

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 160 °C
-DETECTOR: 200 °C
-COLUMN: 115 °C

CARRIER GAS: N_2 or He, 50 mL/min

COLUMN: 1.8 m x 4 mm ID glass; 3% OV-1 on 100/120 mesh Gas-Chrom Q or equivalent

CALIBRATION: 1-octanethiol in acetone

RANGE: 3 to 64 µg per sample

ESTIMATED LOD: not determined

PRECISION (s_r): 0.030 [2]

APPLICABILITY: The working range is 0.05 to 1 ppm (0.3 to 6 mg/m³) for a 10-L air sample.

INTERFERENCES: Presence of other volatile compounds may interfere with collection of 1-octanethiol or reduce capacity of sorbent tube.

OTHER METHODS: None evaluated by NIOSH.

REAGENTS:
1. Acetone*.
2. 1-Octanethiol, ≥ 97% purity.*
3. Calibration stock solution, 0.843 µg/µL. Dissolve 10 µL 1-octanethiol in 10 mL acetone. Prepare fresh daily.
4. Nitrogen, purified.
5. Hydrogen, prepurified.
6. Air, filtered.

*See Special Precautions.

EQUIPMENT:
1. Sampler: glass tube, 8.5 cm long, 6 mm OD, 4 mm ID, sealed with PTFE tape and plastic caps containing front (100-mg) and rear (50-mg) sections of 60/80 mesh Tenax-GC, separated and held in place by three silanized glass wool plugs. (Tenax-GC pretreatment: Sohxlet extraction for 6 hrs with acetone/methanol, 6 hrs with methanol, then drying under vacuum.) Typical pressure drop across tube is 2.4 kPa at 0.05 L/min flow. Similar commercially available tubes, e.g., SKC #226-35-03, are probably acceptable.
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Ultrasonic bath.
4. Gas chromatograph, sulfur-specific FPD, linearizer (if available), integrator and column (page 2510-1).
5. Vials, glass, 2- and 5-mL, crimp seals or caps, PTFE-lined silicone rubber septa.
6. Pipets, 1-, 2- and 5-mL, with pipet bulb.
7. Syringes, 10- and 100-µL.

SPECIAL PRECAUTIONS: Acetone is highly flammable (flash point = -18 °C).

Thiols are malodorous [1]. Prepare samples and standards in well-ventilated hood.

SAMPLING:
1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.05 L/min for a total sample size of 1 to 15 L.
   NOTE: Sample at 0.2 L/min for 15 min for ceiling measurements.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:
5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 2.0 mL acetone to each vial. Attach crimp cap to each vial.
7. Place vials in an ultrasonic bath for 30 min.

CALIBRATION AND QUALITY CONTROL:
8. Calibrate daily with at least five working standards over the range 1 to 60 µg 1-octanethiol per sample.
   a. Add known amounts of calibration stock solution to acetone in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (square root of peak height vs. µg 1-octanethiol).

9. Determine desorption efficiency (DE) at least once for each batch of Tenax-GC used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. µg 1-octanethiol recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2510-1. Inject sample aliquot manually using solvent flush technique or with autosampler. Under these conditions, the retention time of 1-octanethiol is about 3.0 min.
    NOTE: If peak area is above the linear range of the working standards, dilute with acetone, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE) of 1-octanethiol found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of 1-octanethiol in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Measurement precision was determined by analyzing spiked sampling media [2]. The average desorption efficiency was 0.94. The breakthrough volume was greater than 15 L for a concentration of 14.6 mg/m³ at 40 °C and 80% RH. Overall precision, bias and storage stability were determined by sampling and analyzing generated atmospheres. Generated concentrations were independently verified. Reference [2] provides more specific information.

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to n-Alkane Mono Thiols, Cyclohexanethiol, and Benzenethiol, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-123 (1978).

[2] Spafford, R. B., H. K. Dillon, D. H. Love, and W. K. Fowler. Analytical Methods Evaluation and Validation for Vinylidene Fluoride, Vinyl Bromide, Vinyl Fluoride, Benzenethiol, and n-Octanethiol: Research Report for n-Octanethiol and Benzenethiol, NIOSH Contract No. 210-79-0100, Southern Research Institute, Birmingham, AL, available from NTIS, Springfield, VA 22161 (1982).

[3] Weast, R. C., ed. CRC Handbook of Chemistry and Physics, 62nd ed., CRC Press, Boca Raton, FL (1981).

METHOD REVISED BY: R. Alan Lunsford, Ph.D., NIOSH/DPSE; data obtained under NIOSH Contract 210-79-0100.

FORMULA: $(CH_3N\text{-}C_6H_4\text{-})_2Cl_2$; $C_{12}H_{14}N_2Cl_2$

(Paraquat dichloride)

M.W.: 257.16 (M.W. Paraquat = 186.26)

PARAQUAT

METHOD: 5003
ISSUED: 2/15/84

OSHA: 0.5 mg/m³ (skin)
NIOSH: not established; Group I Pesticide [1]
ACGIH: 0.1 mg/m³ (respirable)

PROPERTIES: solid; decomposes @ 175 °C; VP not significant

SYNONYMS: 1,1'-dimethyl-4,4'-bipyridinium dichloride; methyl viologen; CAS # 1910-42-5; 1,1'-dimethyl-4,4'-bipyridinium bis methyl sulfate; CAS #2074-50-2 .

SAMPLING

SAMPLER: FILTER
(1-µm PTFE membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 40 L @ 0.5 mg/m³
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: at least 1 week

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.26 to 1.03 mg/m³ [2]
(90-L samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.088 [2]

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: 1,1-dimethyl-4,4'-bipyridium cation

DESORPTION: 5 mL water

INJECTION: 20 µL

COLUMN: 30 cm x 4 mm ID stainless steel pack with µ-Bondapak C_{18} or equivalent

MOBILE PHASE: 25% acetonitrile; 75% 0.01 M heptane sulfonic acid sodium salt; 1.5 mL/min

DETECTOR: UV absorption @ 254 nm

CALIBRATION: Paraquat dichloride in water

RANGE: 0.02 to 0.5 mg/sample [3]

ESTIMATED LOD: 0.01 mg/sample [3]

PRECISION (s_r): 0.048 [2]

APPLICABILITY: The working range is 0.1 to 2.5 mg/m³ for a 200-L air sample. The Paraquat cation is the analyte for this method; therefore, either salt, the dichloride or bismethyl sulfate, can be quantitated. The standards are prepared from a solution of the dichloride salt with appropriate stoichiometric factor applied.

INTERFERENCES: None identified.

OTHER METHODS: This is Method S294 [3] in a revised format.

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REAGENTS:
1. Water, deionized, distilled.
2. Acetonitrile, HPLC grade.
3. 1-Heptane sulfonic acid sodium salt.
4. Paraquat dichloride.* Dry at 50 °C to remove water of hydration.
5. Calibration stock solution, 0.02 mg Paraquat cation/µL. Dissolve 27.6 mg anhydrous Paraquat dichloride in distilled water to make 10 mL solution. Prepare in duplicate.
6. LC mobile phase, 25% acetonitrile in 0.01 M aqueous 1-heptane sulfonic acid sodium salt.

*See Special Precautions.

EQUIPMENT:
1. Sampler: 1-µm PTFE filter, 37-mm diameter with backup pad in a two-piece filter cassette held together with tape or shrink bands.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. HPLC, UV absorption detector at 254 nm, integrator and column (page 5003-1).
4. Vials, 20-mL, scintillation.
5. Pipets, 5-mL, and microliter pipets or syringe.
6. Syringe, 20-µL, or fixed sample loop or autosampler for injections.
7. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Paraquat is listed as a severe poison. Use care in handling [1,4].

SAMPLING:
1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a total sample size of 40 to 1000 L.

SAMPLE PREPARATION:
3. Carefully transfer the filter from the cassette to a vial using tweezers.
4. Add 5 mL deionized, distilled water to each vial. Cap the vial and gently swirl it to wet the filter completely.

CALIBRATION AND QUALITY CONTROL:
5. Calibrate daily with at least five working standards covering the range 0.01 to 0.5 mg Paraquat per sample.
   a. Add calibration stock solution with a microliter syringe to 5 mL water in a scintillation vial.
   b. Analyze together with samples and blanks (steps 7 through 9).
   c. Prepare calibration graph (response vs. mg Paraquat).
6. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.

MEASUREMENT:
7. Set HPLC to conditions given on page 5003-1.
8. Inject sample aliquot using a syringe, a fixed volume sample loop or an autosampler.
9. Measure peak response.

CALCULATIONS:
10. Read the mass, mg, of Paraquat found on the filter, W, and the average media blank, B, from the calibration graph.

11. Calculate concentration of Paraquat cation, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{(W - B) \cdot 10^3}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method S294 was issued on March 16, 1979, and validated over the range of 0.256 to 1.03 mg/m^3 using a 90-L sample [2,6]. The overall precision, s_r, was 0.0691 with an average recovery of 98.2%, representing a non-significant bias. The concentration of Paraquat in the generation system was verified by an independent method [5]. Recovery was 100% in the range 23.7 to 94.6 µg per sample. Collection efficiency of the filter was determined by collecting six filter samples at about 1.8 mg/m^3 for a 90-L sample. The sampler consisted of two filters per cassette arranged so that the back filter was supported by the backup pad and the front filter was separated from the back filter. The overall collection efficiency was 100%. Samples were stored at room temperature for one week and found to be stable.

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Manufacturing and Formulation of Pesticides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-174 (1978).
[2] NIOSH Backup Data Report S294 (unpublished, March, 1979), available as "Ten NIOSH Analytical Methods," Order No. PB 81-229 684 from NTIS, Springfield, VA 22161.
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 5, S294, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[4] Aldrich Catalog/Handbook of Fine Chemicals (1982-83).
[5] Chevron Chemical Company, Paraquat by Colorimetry, AM-8-1086 (April 7, 1977).
[6] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY: Edward Slick, NIOSH/DPSE; S294 originally validated under NIOSH Contract 210-76-0123.

FORMULA: C_6H_5OH: C_6H_6O

M.W.: 94.11

PHENOL

METHOD: 3502
ISSUED: 2/15/84

OSHA: 5 ppm
NIOSH: 20 mg/m³; 60 mg/m³/15 min [1]
ACGIH: 5 ppm (skin); STEL 10 ppm
(1 ppm = 3.85 mg/m³)

PROPERTIES: solid; d 1.071 g/mL @ 25 °C;
MP 41 °C; BP 182 °C;
VP 47 Pa (0.35 mm Hg; 460 ppm) @ 25 °C;
explosive range 1.7 to 8.6% (v/v) in air

SYNONYMS: carbolic acid; CAS #108-95-2.

SAMPLING

SAMPLER: BUBBLER
(0.1 N sodium hydroxide)

FLOW RATE: 0.2 to 1 L/min

VOL-MIN: 26 L
-MAX: 240 L

SHIPMENT: hand delivery or special bubbler shipping cases

SAMPLE STABILITY: at least 5 days @ 25 °C [2]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 9.5 to 38 mg/m³ [2]
(100-L samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.068 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: phenol

pH ADJUSTMENT: 0.1 mL conc. sulfuric acid;
pH < 4

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 215 °C
-DETECTOR: 225 °C
-COLUMN: 200 °C

CARRIER GAS: N_2 or He, 50 mL/min

COLUMN: stainless steel, 1.2 m x 6 mm OD,
35/60 mesh Tenax or equivalent

CALIBRATION: phenol in 0.1 N sodium hydroxide

RANGE: 0.5 to 6 mg [3]

ESTIMATED LOD: 10 µg per sample [4]

PRECISION (s_r): 0.044 [2]

APPLICABILITY: The working range is 5 to 60 mg/m³ for a 100-L air sample [1]. This method may be used for STEL measurements (15-L samples).

INTERFERENCES: None identified. Ethanol does not interfere.

OTHER METHODS: This is Method S330 in a revised format [3]; the method also appears in the phenol criteria document [1].

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REAGENTS:
1. Phenol.*
2. Water, distilled.
3. Sulfuric acid, conc.
4. Calibration stock solution, 0.5 mg/mL. Dissolve 50 mg phenol (accurately weighed) in 0.1 N sodium hydroxide in a 100-mL volumetric flask. Dilute to 100 mL.
5. Collection medium, 0.1 N sodium hydroxide. Dissolve 4.0 g sodium hydroxide in distilled water. Dilute to 1 L.
6. Nitrogen, purified.
7. Hydrogen, purified.
8. Air, filtered, compressed.

*See Special Precautions.

EQUIPMENT:
1. Sampler: glass midget bubbler.*
2. Personal sampling pump, 0.2 to 1 L/min, with splashover protection and flexible connecting tubing.
3. Gas chromatograph with glass-lined injection port, FID, integrator and column (page 3502-1).
4. Syringe, 10-µL, readable to 0.1 µL.
5. Volumetric flasks, 25- and 100-mL.*
6. Pipets, 0.1-, 0.5-, 1-, 2-, 4-, 8- and 15-mL, graduated in 0.1-mL increments, with pipet bulb.*
7. pH paper.
8. Glass wool.

*Wash with detergent; rinse thoroughly with distilled water.

SPECIAL PRECAUTIONS: Phenol is a severe poison and is corrosive [1]. Use protective equipment when handling. All work should be performed in a hood.

SAMPLING:
1. Calibrate each personal sampling pump with a sampler and glass wool-packed splashover tube in line.
2. Pipette 15 mL 0.1 N sodium hydroxide into each midget bubbler.
3. Connect a splashover tube between the midget bubbler and the personal sampling pump using short pieces of flexible tubing.
4. Sample at 0.2 to 1 L/min for a total sample size of 26 to 240 L.
5. After sampling, remove and tap the bubbler stem gently against the inside wall of the bubbler bottle. Rinse the stem with 1 mL distilled water, adding the wash to the bubbler. Seal the bubbler with a hard, non-reactive stopper (PTFE or glass, not rubber) to prevent leakage during shipping.

SAMPLE PREPARATION:
6. Transfer the solution from the bubbler to a 25-mL volumetric flask.
7. Rinse the bubbler twice with 1 mL distilled water and add the rinses to the flask.
8. Add 0.1 mL conc. H_2SO_4 to the flask and mix. Use pH paper to make sure that the pH is less than 4.
9. Dilute to the mark with distilled water and mix.

CALIBRATION AND QUALITY CONTROL:
10. Calibrate daily with at least five working standards covering the range of the samples:
    a. Pipet, e.g., 0, 0.5, 1.0, 2.0, 4.0, 8.0 and 15 mL calibration stock solution into 25-mL volumetric flasks. Add the appropriate amount of 0.1 N sodium hydroxide with a graduated pipette to reach a 15-mL volume for each of the working standards.

b. Add 0.1 mL conc. H_2SO_4 to each standard. Make up to 25 mL with distilled water.
c. Check the solution with pH paper to make sure that its pH is less than 4.
d. Analyze the working standards and blanks under the same GC conditions and during same time period as samples.
e. Prepare a calibration graph by plotting peak area vs. mg phenol in the 25 mL volume.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 3502-1.
12. Inject a sample aliquot using solvent flush technique. Make duplicate injections of samples and standards. Measure peak area.
13. Clean the glass inlet on the GC at the end of each day with water and acetone rinses. Reinsert the glass inlet into the injection port and let it bake out overnight.

CALCULATIONS:

14. Read the mass (mg) of phenol found in the sample bubbler (W) and average blank bubblers (B) corresponding to each peak area from the calibration graph.
15. Calculate concentration, C (mg/m^3), of phenol in the air volume sampled, V (L):

$$C = \frac{(W - B) \cdot 10^3}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method S357 [3] was issued on August 1, 1975, and validated over the range 9.46 to 37.8 mg/m^3 at 22 °C and 760 mm Hg, using a 100-L sample [2]. Overall precision, s_r, was 0.068, determined by sampling and analyzing generated atmospheres containing 9.46, 18.9 and 37.8 mg/m^3 phenol in air. The concentrations were determined from the delivery rate of the syringe drive pump and the flow rates of the dilution air (20.1 L/min). The collection efficiency of the bubbler was determined at 37.8 mg/m^3 and found to be 1.00 $\pm$ 0.01. No concentration changes occurred after five days storage of six samples of 15 mL 0.1 N sodium hydroxide in 25-mL volumetric flasks spiked with 1.9 mg phenol. Recovery at the OSHA standard level was 97.4%; this was not considered to be a significant bias.

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Phenol, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-196 (1976).
[2] Documentation of the NIOSH Validation Tests, S330, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3, S330, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[4] UBTL Memorandum, Analytical Laboratory Report for Phenol, Sequence #2660-N and 2340-J (December 8, 1980 and June 25, 1980).

METHOD REVISED BY: Julie R. Okenfuss, NIOSH/DPSE; S357 originally validated under NIOSH Contract CDC-99-74-45.

POLYCHLOROBIPHENYLS

FORMULA: mixture: $C_{12}H_{10-x}Cl_x$ [where x = 1 to 10]
M.W.: ca. 258 (42% Cl ; $C_{12}H_7Cl_2$)
ca. 326 (54% Cl ; $C_{12}H_5Cl_5$)

METHOD: 5503
ISSUED: 2/15/84

OSHA: 1 mg/m³ (42% Cl); 0.5 mg/m³ (54% Cl)
NIOSH: 0.001 mg/m³ [1,2]
ACGIH: 1 mg/m³ (42% Cl); STEL 2 mg/m³
0.5 mg/m³ (54% Cl); STEL 1 mg/m³ (skin)

PROPERTIES: 42% Cl: BP 325 to 366 °C; MP -19 °C; d 1.38 g/mL @ 25 °C; VP 0.01 Pa (8 x 10^{-5} mm Hg; 1 mg/m³) @ 20 °C [3]
54% Cl: BP 365 to 390 °C; MP 10 °C; d 1.54 g/mL @ 25 °C; VP 0.0004 Pa (3 x 10^{-6} mm Hg; 0.05 mg/m³) @ 20 °C [3]

SYNONYMS: PCB; CAS #1336-36-3; 1,1'-biphenyl chloro (CAS #27323-18-8); chlorodiphenyl, 42% Cl (Aroclor 1242; CAS #53469-21-9), and 54% Cl (Aroclor 1254; CAS #11097-69-1)

SAMPLING

SAMPLER: FILTER + SOLID SORBENT (13-mm glass fiber + Florisil, 100 mg/50 mg)

FLOW RATE: 0.05 to 0.2 L/min

VOL-MIN: 1 L @ 0.5 mg/m³
-MAX: 50 L

SHIPMENT: transfer filters to glass vials after sampling

SAMPLE STABILITY: unknown for filters; 2 months for Florisil tubes [4]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: none identified

OVERALL PRECISION (s_r): not evaluated

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ECD (^{63}Ni)

ANALYTE: polychlorobiphenyls

DESORPTION: filter + front section, 5 mL hexane; back section, 2 mL hexane

INJECTION VOLUME: 4 µL with 1-µL backflush

TEMPERATURE-INJECTION: 250 - 300 °C
-DETECTOR: 300 - 325 °C
-COLUMN: 180 °C

CARRIER GAS: N_2, 40 mL/min

COLUMN: glass, 1.8 m x 2 mm ID, 1.5% OV-17/1.95% QF-1 on 80/100 mesh Chromosorb WHP

CALIBRATION: commercial PCB mixture in hexane

RANGE: 0.4 to 4 µg per sample [5]

ESTIMATED LOD: 0.03 µg per sample [5]

PRECISION (s_r): 0.044 [4]

APPLICABILITY: The working range is 0.01 to 10 mg/m³ for a 40-L air sample [4].

INTERFERENCES: Chlorinated pesticides, such as DDT and DDE, may interfere with quantitation of PCB. Sulfur-containing compounds in petroleum products also interfere [6].

OTHER METHODS: This method combines and replaces Methods S120 [7] and P&CAM 244 [4]. Methods S121 [8] and P&CAM 253 [9] for PCB have not been revised.

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REAGENTS:

1. Hexane, pesticide quality.
2. Florisil, 30/48 mesh sieved from 30/60 mesh. After sieving, dry at 105 °C for 45 min. Mix the cooled Florisil with 3% (w/w) distilled water.
3. Nitrogen, purified.
4. Stock standard solution of the PCB in methanol or isooctane (commercially available).*

*See Special Precautions.

EQUIPMENT:

1. Sampler: 13-mm glass fiber filter without binders in a Swinnex cassette (Cat. No. SX 0001300, Millipore Corp.) followed by a glass tube, 7 cm long, 6 mm OD, 4 mm ID containing two sections of 30/48 mesh deactivated Florisil. The front section is preceded by glass wool and contains 100 mg and the backup section contains 50 mg; urethane foam between sections and behind the backup section. Join the cassette and Florisil tube with PVC tubing, 3/8" L x 9/32" OD x 5/32" ID, on the outlet of the cassette and with another piece of PVC tubing, 3/4" L x 5/16" OD x 3/16" ID, complete the union.
2. Personal sampling pump, 0.05 to 0.2 L/min, with flexible connecting tubing.
3. Tweezers.
4. Vials, glass, 4- and 7-mL, with aluminum or PTFE-lined caps.
5. Gas chromatograph, electron capture detection (^{63}Ni), integrator and column (page 5503-1).
6. Volumetric flasks, 10-mL and other convenient sizes for preparing standards.
7. Syringe, 10-µL.

SPECIAL PRECAUTIONS: Avoid prolonged or repeated contact of skin with PCB and prolonged or repeated breathing of the vapor [1,2, 10].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.05 and 0.2 L/min for a total sample size of 1 to 50 L.
4. Transfer the glass fiber filters to 7-mL vials. Cap the Florisil tubes with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the glass wool and 100-mg Florisil bed in the same 7-mL vial in which the filter was stored. Add 5.0 mL hexane.
6. In a 4 mL vial, place the 50-mg Florisil bed including the two urethane plugs. Add 2.0 mL hexane.
7. Allow to stand 20 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 10 to 500 ng PCB/mL.
   a. Add known amounts of stock standard solution to hexane in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 10 and 11).
   c. Prepare calibration graph (sum of areas of selected peaks vs. ng PCB/mL).
9. Determine desorption efficiency (DE) at least once for each lot of glass fiber filters and Florisil used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank Florisil tube.
   b. Inject known amounts of stock standard solution directly onto front sorbent section and onto a media blank filter with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. ng PCB recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 5503-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE 1: Where individual identification of PCB is needed, a procedure using a capillary column may be used [11].
    NOTE 2: If peak area is above the linear range of the working standards, dilute with hexane, reanalyze and apply the appropriate dilution factor in calculations.
12. Sum the areas for five or more selected peaks.

CALCULATIONS:

13. Determine the mass, ng (corrected for DE) of PCB found on the glass fiber filter (W) and in the Florisil front (W_f) and back (W_b) sorbent sections, and in the average media blank filter (B) and front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of PCB in the air volume sampled, V (L):

$$C = \frac{(W+W_f + W_b - B-B_f - B_b)\cdot 10^{-3}}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method uses 13-mm glass fiber filters which have not been evaluated for collecting PCB. In Method S120, however, Aroclor 1242 was completely recovered from 37-mm glass fiber filters using 15 mL isooctane [7,12,13]. With 5 mL of hexane, Aroclor 1016 was also completely recovered from 100-mg Florisil beds after one-day storage [4]. Thus, with no adsorption effect likely on glass fiber filters for PCB, 5 mL hexane should be adequate to completely extract PCB from combined filters and front sorbent sections. Sample stability on glass fiber filters has not been investigated. Breakthrough volume was >48 L for the Florisil tube at 75% RH in an atmosphere containing 10 mg/m³ Aroclor 1016 [4].

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Polychlorinated Biphenyls, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-225 (1977).
[2] Current Intelligence Bulletin 7, Polychlorinated Biphenyls (PCBs), U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-127 (1975).

[3] Hutzinger, O. S. Safe and V. Zitko. The Chemistry of PCBs, CRC Press, Inc., Cleveland, OH (1974).
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[5] User check, Southern Research Institute, NIOSH Sequence #4121-U (unpublished, January 25, 1984).
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[9] Ibid, Vol. 1, P&CAM 253.
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[11] Dunker, J. C. and M. T. J. Hillebrand. Characterization of PCB Components in Clophen Formulations by Capillary GC-MS and GC-ECD Techniques, Environ. Sci. Technol., 17 (8), 449-456 (1983).
[12] Backup Data Report for S120, prepared under NIOSH Contract 210-76-0123, available as "Ten NIOSH Analytical Methods, Set 2," Order No. PB 271-464 from NTIS, Springfield, VA 22161.
[13] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY: James E. Arnold, NIOSH/DPSE; S120 originally validated under NIOSH Contract 210-76-0123.

Table 1. Composition of some Aroclors [3].

Major Components	Aroclor 1016	Aroclor 1242	Aroclor 1254
Biphenyl	<0.1%	<0.1%	<0.1%
Monochlorobiphenyls	1	1	<0.1
Dichlorobiphenyls	20	16	0.5
Trichlorobiphenyls	57	49	1
Tetrachlorobiphenyls	21	25	21
Pentachlorobiphenyls	1	8	48
Hexachlorobiphenyls	<0.1	1	23
Heptachlorobiphenyls	none detected	<0.1	6
Octachlorobiphenyls	none detected	none detected	none detected

FORMULA: $C_{23}H_{22}O_6$

M.W.: 394.43

ROTENONE

METHOD: 5007
ISSUED: 2/15/84

OSHA: 5 mg/m³
NIOSH: Group II Pesticide [1]
ACGIH: 5 mg/m³, STEL 10 mg/m³

PROPERTIES: solid, MP 163 °C or 181 °C;
BP 220 °C @ 0.5 mm Hg;
d ca. 1 g/cm³;
VP not significant

SYNONYMS: tubatoxin; cube; CAS# 83-79-4.

SAMPLING

SAMPLER: FILTER
(1-µm PTFE membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 8 L
-MAX: 400 L

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days @ 25 °C
in dark

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: desirable; 1 g

ACCURACY

RANGE STUDIED: 1 to 11 mg/m³ [3]
(100-L sample)

BIAS: not significant [3]

OVERALL PRECISION (s_r): 0.079 [3]

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: Rotenone

EXTRACTION: 4 mL acetonitrile; 30 min

INJECTION VOLUME: 10 µL

MOBILE PHASE: 60% methanol/40% water, 2 mL/min

DETECTOR: UV @ 290 nm; 0.1A full-scale; 1 cm cell

COLUMN: µ-Bondapak C_{18} (30 cm x 3.9 mm ID stainless steel); ambient temperature

CALIBRATION: solutions of Rotenone in acetonitrile

RANGE: 0.04 to 1 mg per sample

ESTIMATED LOD: 4 µg per sample [2,3]

PRECISION (s_r): 0.024 [3]

APPLICABILITY: The working range is 0.4 to 10 mg/m³ for a 100-L air sample and the method is applicable to commercial formulations.

INTERFERENCES: None known. Rotenone, a naturally occurring insecticide, is adequately separated by HPLC from other compounds (e.g., sumatrol, α-toxicarol, deguelin, elliptone, malaccol, and tephrosin [4]) present in commercial cube root extracts [5]. Rotenone is sensitive to photodecomposition.

OTHER METHODS: This is Method S300 [2] in a revised format.

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REAGENTS:

1. Acetonitrile, HPLC grade.*
2. Methanol, HPLC grade.
3. Rotenone, 97% purity.
4. Water, distilled, HPLC grade.
5. Calibration stock solution, 3 mg/mL. Dissolve 0.075 g Rotenone in 25 mL acetonitrile. Prepare fresh daily in duplicate.
6. Recovery stock solution, 50 mg/mL. Dissolve 0.500 g rotenone in acetone. Dilute to 10 mL. Prepare fresh daily.

*See Special Precautions.

EQUIPMENT:

1. Sampler: 37-mm, two-piece cassette containing 1-µm PTFE membrane filter with backup pad.
   NOTE: Use an opaque cassette or otherwise shield the filter from light to minimize photodecomposition of Rotenone during and after sampling.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. HPLC, UV detector, integrator and column (page 5007-1).
4. Jars, ointment, 60-mL, with PTFE-lined caps.
5. Vials, 4-mL, with PTFE-lined caps.
6. Filtration device, Swinney 13-mm or equivalent with 1-µm PTFE filters.
7. Volumetric, 10- and 25-mL.
8. Syringes, microliter, for sample injection and standard preparation.
9. Pipet, 4-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Avoid breathing acetonitrile vapors; may cause skin irritation.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 8 to 400 L. Do not exceed 2 mg total dust loading on the filter.
3. Collect a bulk sample (1 g) in a glass vial with PTFE-lined cap; ship separately from filters.

SAMPLE PREPARATION:

4. Open filter cassette; transfer filter to 60-mL jar.
5. Add 4.0 mL acetonitrile; gently swirl for 30 min.
6. Filter each sample using the Swinney filter holder and 5-mL syringe. Deliver filtrate to a 4-mL vial.

CALIBRATION AND QUALITY CONTROL:

7. Prepare at least five working standards daily in the range 0.01 to 1 mg Rotenone per sample.
   a. Add known amounts of calibration stock solution to acetonitrile in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 9 and 10).
   c. Prepare calibration graph (peak area vs. mg Rotenone.
8. Check recovery with at least three spiked media blanks per sample set in the calibration range (step 7).
   a. Add aliquots of recovery stock solution to blank filters with a microliter syringe. Air dry.
   b. Analyze together with working standards (steps 4 through 6, 9 and 10).
   c. Calculate recovery [(mg recovered - mg blank)/mg added].

MEASUREMENT:

9. Set HPLC system to conditions given on page 5007-1. Inject 10-µL sample.
10. Measure peak area.

CALCULATIONS:

11. Read the mass, mg (corrected for recovery) of Rotenone found on the filter (W) and average media blank (B) from the calibration graph.
12. Calculate the concentration, C (mg/m^3), of Rotenone in the air volume sampled, V (L):

$$C = \frac{(W - B) \cdot 10^3}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method S300 [2] was issued on May 11, 1979, and validated over the range 1.16 to 11.1 mg/m^3 at 25 °C and 760 mm, using 100-L samples [3,6]. Overall precision, s_r, was 0.079 with average recovery 100.4%, representing a non-significant bias. The concentration of Rotenone (generated by Wright dust feeder using Ortho Rotenone Dust [1%; Chevron Chemical Co.] enriched to 10% Rotenone with analytical grade Rotenone [Aldrich Chemical Co.]) was independently verified by collection in dioxane and HPLC analysis. Recovery was 0.98 in the range 250 to 1000 µg Rotenone per sample. Collection efficiency of the PTFE filter was found to be greater than 99% and no detectable Rotenone (LOD = 4 µg) was found on Chromosorb 102 tubes placed behind the PTFE filters at 11.8 mg/m^3. No loss was seen from spiked filters stored in the dark at room temperature for seven days.

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure During Manufacture and Formulation of Pesticides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-174 (1978).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 5, S300, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
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[5] Bushway, R. J., B. S. Engdahl, B. M. Colvin, and A. R. Hanks. J. Assoc. Official Anal. Chemists, 58, 965 (1975).
[6] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY: Jerome Smith, Ph.D., NIOSH/DPSE; S300 originally validated under NIOSH Contract 210-76-0123.

FORMULA: SiO_2

M.W.: 60.08

SILICA, crystalline, respirable

METHOD: 7500
ISSUED: 2/15/84

OSHA & ACGIH : Quartz (respirable), 10 mg/m³/(% SiO_2 + 2); Cristobalite and Tridymite (respirable), 1/2 the above

NIOSH: 0.05 mg/m³ [1]

PROPERTIES: solid; d 2.65 g/cm³ @ 0 °C; Crystalline transformations: quartz to tridymite @ 867 °C; tridymite to cristobalite @ 1470 °C; α-quartz to ß-quartz @ 573 °C

SYNONYMS: free crystalline silica; silicon dioxide; CAS #14808-60-7 (quartz), CAS #14464-46-1 (cristobalite), CAS #15468-32-3 (tridymite).

SAMPLING

SAMPLER: CYCLONE + FILTER (10-mm nylon cyclone + 5-µm PVC membrane)

FLOW RATE: 1.7 L/min

VOL-MIN: 800 L @ 0.05 mg/m³
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: high-volume respirable (preferred) or settled dust; to identify interferences

ACCURACY

RANGE STUDIED: 25 to 2500 µg/m³

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.09 (50 to 200 µg)

MEASUREMENT

TECHNIQUE: X-RAY POWDER DIFFRACTION

ANALYTE: crystalline silica

ASH: muffle furnace or RF plasma asher or dissolve in tetrahydrofuran

REDEPOSIT: on 0.45 µm Ag membrane filter

XRD: Cu target X-ray tube, graphite monochromator
Optimize for intensity; 1° slit
Slow step scan, 0.02°/10 sec
Integrated intensity with background subtraction

CALIBRATION: suspensions of silica in 2-propanol

RANGE: 0.04 to 2 mg per sample

ESTIMATED LOD: 5 µg per sample [3]

PRECISION (s_r): 0.08 (50 to 200 µg) [2]

APPLICABILITY: The working range is 0.05 to 2.5 mg/m³ for an 800-L air sample.

INTERFERENCES: Micas, potash, feldspars, zircon, graphite, and aluminosilicates. See APPENDIX.

OTHER METHODS: This is P&CAM 259 [4] which has been collaboratively tested [2]. This method is similar, except for sample collection, to S315 [5,6]. Method P&CAM 109 [7,8,9], which incorporates an internal standard, has been dropped. Colorimetry (Method 7601 [10]) is an alternate measurement procedure, as is IR spectrometry (Method 7602).

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REAGENTS:

1. Quartz* (SRM 1878, available from Office of Standard Reference Materials, B311 Chemistry Building, National Bureau of Standards, Washington, DC 20234); Cristobalite* and Tridymite* (available from NIOSH, DPSE, MRB, 4676 Columbia Parkway, Cincinnati, OH 45226).
2. 2-Propanol.
3. Desiccant.
4. Glue or tape for securing Ag filters to XRD holders.
5. Optional: tetrahydrofuran (THF)* (if LTA or muffle furnace are unavailable).
6. Optional (if calcite present): 25% v/v concentrated hydrochloric acid (ACS reagent grade) in distilled water and 25-mm filters of PVC or cellulose ester with pore size of 1 µm or less.

*See Special Precautions.

EQUIPMENT:

1. Personal sampler: 10-mm nylon cyclone; polyvinyl chloride (PVC) membrane filters, 37-mm diameter, 5-µm pore size; two-piece filter cassette.
   NOTE: Gelman VM-1 filters are unacceptable because of high ash and background. Gelman GLA-5000 and FWS-B filters (MSA) are suitable if THF dissolution must be used.
2. Personal sampling pump, 1.7 L/min, with flexible connecting tubing.
3. High-volume sampler: 0.5-inch HASL cyclone; PVC membrane filters, 37-mm diameter, 5-µm pore size; three-piece filter cassette; with high-volume pump, 9 L/min.
4. Silver membrane filters, 25-mm diameter, 0.45-µm pore size (Selas Flotronics, Dresher, PA 19006).
5. X-ray powder diffractometer equipped with copper target X-ray tube, graphite monochromator and scintillation detector.
6. Reference specimen (mica, Arkansas stone or other stable standard) for data normalization.
7. Low temperature radio frequency plasma asher or muffle furnace.
8. Membrane filtration apparatus and side arm vacuum flask with a 25-mm filter holder.
9. Sieve, 10-µm, for wet sieving.
10. Analytical balance (0.01 mg); magnetic stirrer; ultrasonic bath or probe; volumetric pipettes and flasks; Pyrex crucibles with covers (muffle furnace); desiccator; reagent bottles with ground glass stoppers; drying oven; polyethylene wash bottle.

SPECIAL PRECAUTIONS: Avoid inhaling silica dust [1].

THF is extremely flammable and should be used in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump to 1.7 L/min with a representative sampler in line.
2. Sample at 1.7 L/min for a total sample size of 800 to 1000 L. Do not exceed 2 mg dust loading on the filter.
   NOTE: Do not allow the sampler assembly to be inverted at any time. Turning the cyclone to anything more than a horizontal orientation may deposit over-sized material from the cyclone body onto the filter.
3. Take a high volume respirable dust sample (e.g., 4 m^3 at 9 L/min).

SAMPLE PREPARATION:

4. Prepare the high-volume respirable dust or settled dust sample for qualitative analysis. The respirable dust sample need only be transferred to a filter and XRD sample holder by: (1) ashing and redepositing as described below for personal samples, or (2) removing part of the dust from a thickly-coated sample and redepositing it, or, (3) by simply mounting all or part of the collection filter on the holder. The settled dust may be ground and/or wet sieved to best match the airborne dust exposure. Wet-sieving is done with a 10-µm sieve, 2-propanol, and an ultrasonic bath [11], followed by evaporation of excess alcohol, drying in an oven for 2 hours, and overnight storage in a dessicator. The end product can be deposited on a filter or packed in a conventional XRD powder holder.
   NOTE: For quantitative determination of percent silica, weigh out, in triplicate, 2 mg of the respirable or sieved dust, transfer to a 50-mL beaker, add 10 mL 2-propanol, and continue with step 6.
5. Use one of the following methods to ash filter samples and blanks:
   a. Low Temperature Ashing: Place the filters in 50-mL beakers within the low temperature asher so that the sample exposure to the plasma is optimized. Ash according to manufacturer's instructions. After ashing, carefully add 15 mL of 2-propanol to each beaker; or
   b. Muffle Furnace Ashing: Wash the filters with 25% v/v hydrochloric acid if the samples contain a significant amount of calcite (greater than 20% of the total dust loading); otherwise, proceed to the next paragraph. Place a 0.5-µm, 25-mm PVC filter in the filtration apparatus and clamp the filter funnel over it. Remove the sample filter from the cassette, fold and drop it on the 25-mm filter. Add 10 mL HCl solution and 5 mL of 2-propanol to the filter funnel and allow to sit for 5 min. Apply vacuum and slowly aspirate the acid and alcohol in the funnel, washing with three successive 10-mL portions of distilled water. Release the vacuum. Carry both filters through the ashing step together.
      Place the filter samples in porcelain crucibles, loosely cover and ash in muffle furnace for 2 hrs at 600 °C (800 °C if graphite is present). Add several mL of 2-propanol to the ash, scrape the crucible with a glass rod to loosen all particles and transfer the residue to a 50-mL beaker. Wash the crucible several more times and add wash to beaker. Add 2-propanol to the beaker to bring the volume to about 15 mL; or
   c. Filter Dissolution: Place the filter in a 40-mL wide-mouth centrifuge tube with 10 mL THF. Place the centrifuge tube in an ultrasonic bath for 10 min. The filter should dissolve almost instantaneously in THF. Continue with the procedure given below at step 6 substituting THF for 2-propanol and centrifuge tube for beaker.
6. Cover the beaker with a watchglass and agitate in an ultrasonic bath for at least 3 min. Observe the suspension to make sure that the agglomerated particles are broken up. Wash the underside of the watchglass with 2-propanol, collecting the washings in the beaker.
7. Place a silver filter in the filtration apparatus. Attach the funnel securely over the entire filter circumference. With no vacuum, pour 2 to 3 mL of 2-propanol onto the filter. Pour the sample suspension from the beaker into the funnel and apply vacuum. During filtration, rinse the beaker several times and add rinsings to the funnel.
8. Control the filtration rate to keep the liquid level in the funnel near the top during rinsing. Do not wash the walls or add 2-propanol to the funnel when the liquid level is lower than 4 cm above the filter. Leave the vacuum on after filtration to produce a dry filter. Remove the filter with forceps and mount it in the XRD sample holder.

CALIBRATION AND QUALITY CONTROL:

9. Prepare and analyze standard filters.
   a. Prepare two suspensions of each analyte in 2-propanol by weighing 10 and 50 mg of the dry powder to the nearest 0.01 mg. Quantitatively transfer each to a 1-L glass-stoppered bottle using 1.00 L of 2-propanol.
      NOTE: Min-U-Sil 5 may be used as a quartz standard without sieving. For cristobalite and tridymite, wet sieve the standard material through a 10-µm sieve with 2-propanol. Evaporate the alcohol. Dry all standards in a 110 °C oven for 4 hrs, cool and store in a desiccator.
   b. Suspend the powder in 2-propanol with an ultrasonic probe or bath for 20 min. Immediately move the flask to a magnetic stirrer with thermally-insulated top and add a stirring bar. Cool to room temperature before withdrawing aliquots.
   c. Mount a filter on the filtration apparatus. Place several mL 2-propanol on the filter. Turn off the stirrer and shake vigorously by hand. Immediately remove the lid and withdraw an aliquot from the center of the 10 mg/L or 50 mg/L suspension. Do not adjust the volume in the pipet by expelling part of the suspension. If more than the desired aliquot is withdrawn, return all of the suspension to the bottle, rinse and dry the pipet, and take a new aliquot. Transfer the aliquot from the pipet to the filter, keeping the tip of the pipet near the surface but not submerged in the delivered suspension.
   d. Rinse the pipet with several mL 2-propanol, draining the rinse into the funnel. Repeat the rinse several more times.
   e. Apply vacuum and rapidly filter the suspension. Leave vacuum on until filter is dry. Do not wash down the sides of the funnel after the deposit is in place since this will rearrange the material on the filter. Transfer the filter to the diffractometer sample mount. Prepare working standard filters, in triplicate, by this technique, at e.g., 20, 30, 50 100, 200 and 500 µg.
   f Analyze by the working standards together with samples and blanks (step 12). The XRD intensities for the working standards (12.d) are designated I_x^o and are then normalized (12.e) to obtain $\hat{I}_x^o$. The intensities for working standards greater than 200 µg should be corrected for matrix absorption (12.f and 13).
   g. Prepare a calibration graph by plotting $\hat{I}_x^o$, vs. µg of each standard.
      NOTE: Poor repeatability (> 10% above 0.04 mg silica) at any given level indicates that new standards should be made. The data should lie along a straight line. A weighted least squares ($1/\sigma^2$ weighting) is preferable.
   h. Determine the slope, m, of the calibration graph in counts/µg. The intercept, b, on the abscissa should be within $\pm$ 5 µg of zero.
      NOTE: A large intercept indicates an error in determining the background, i.e., an incorrect baseline or interference by another phase.
10. Select six silver membrane filters as media blanks randomly from the same box of filters to be used for depositing the samples. These will be used to test for sample self-absorption. Mount each of the media blanks on the filtration apparatus and apply vacuum to draw 5 to 10 mL of 2-propanol through the filter. Remove, let dry and mount on XRD holders. Determine the net normalized count for the silver peak, $\hat{I}_{Ag}^o$, for each media blank (step 12). Obtain an average value for the six media blanks.

MEASUREMENT:

11. Obtain a qualitative X-ray diffraction scan (e.g., 10 to 80 degrees 2-theta) of the high-volume respirable sample (or bulk settled dust) to determine the presence of free silica polymorphs and interferences (see APPENDIX). The expected diffraction peaks are:

	Peak (2-Theta Degrees)		
Mineral	Primary	Secondary	Tertiary
Quartz	26.66	20.85	50.16
Cristobalite	21.93	36.11	31.46
Tridymite	21.62	20.50	23.28
Silver	38.12	44.28	77.47

12. Perform the following for each sample, working standard, and blank filter:
    a. Mount the reference specimen. Determine the net intensity, I_r, of the reference specimen before and after each filter is scanned. Use a diffraction peak of high intensity that can be rapidly but reproducibly (s_r <0.01) measured.
    b. Mount the sample, working standard, or blank filter. Measure the diffraction peak area for each silica polymorph. Scan times must be long, e.g., 15 min.
    c. Measure the background on each side of the peak for one-half the time used for peak scanning. The sum of these two counts is the average background. Determine the position of the background for each sample.
    d. Calculate the net intensity, I_x, (the difference between the peak integrated count and the total background count).
    e. Calculate and record the normalized intensity, $\hat{I}_x$, for the sample peak on each sample, field blank and standard:

$$\hat{I}_x = \frac{I_x}{I_r} \cdot N.$$

    NOTE: Select a convenient normalization scale factor, N, which is approximately equivalent to the net count for the reference specimen peak, and use this value of N for all analyses. Normalizing to the reference specimen intensity compensates for long-term drift in X-ray tube intensity. If intensity measurements are stable, the reference specimen may be run less frequently and the net intensities should be normalized to the most recently-measured reference intensity.
    f. Determine the normalized count, $\hat{I}_{Ag}$, of an interference-free silver peak on the sample filter following the same procedure. Use a short scan time for the silver peak (e.g., 5% of scan time for analyte peaks) throughout the method.
    g. Scan each field blank over the same 2-θ range used for the analyte and silver peaks. These analyses serve only to verify that contamination of the filters has not occurred. The analyte peak should be absent. The normalized intensity of the silver peak should match that of the media blanks.

CALCULATIONS:

13. Calculate the concentration of silica, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{\hat{I}_X \cdot f(T) - b}{m \cdot V}, \ mg/m^3$$

where:

$\hat{I}_X$ = normalized intensity for sample peak

b = intercept of calibration graph ($\hat{I}^0_X$ vs. W)

m = slope of calibration graph, counts/µg

$f(T) = \frac{-R \ln T}{1 - T^R}$ = absorption correction factor (Table 1)

$R = \sin(\Theta_{Ag})/\sin(\Theta_X)$

$T = \hat{I}_{Ag}/(\text{average } \hat{I}^0_{Ag})$ = transmittance of sample

$\hat{I}_{Ag}$ = normalized silver peak intensity from sample

average $\hat{I}^0_{Ag}$ = normalized silver peak intensity from media blanks (average of six values)

NOTE: For a more detailed discussion of the absorption correction procedure, see references 12 through 17.

EVALUATION OF METHOD:

This method is based on P&CAM 259 which was collaboratively tested [2]. The testing included a ruggedization step to test the effects of the use of muffle furnace or plasma asher (but not the use of THF), shipment of samples, ashing time, sonification time and others. None of these factors was found to have an effect. The method was shown to have no bias when referenced to the Talvitie spectrophotometric method [10] and when all standards and samples were Min-U-Sil 5. The relative standard deviations for intralaboratory, total measurement and overall (including sampling) variability are:

Measurement Precision, s_r:

Intralaboratory:	50 to 200 µg	0.08 [1]
	20 µg	0.20 [5]
	10 µg	0.28 [18]
Total (intra- and interlaboratory):	50 to 200 µg	0.17 [1]

Overall Precision, s_r:

Total (intra- and interlaboratory):	50 to 200 µg	0.29 [2]

The use of THF for dissolving the collection filter is not a well established technique for silica, but preliminary data are available on samples from the NIOSH Proficiency Analytical Testing (PAT) Program. On 40 such samples analyzed over a period of one year, results averaged 95% of the geometric mean of all the participating laboratories. The precision for three analysts using THF approximated the total measurement error given above [18].

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METHOD REVISED BY: M. T. Abell; D. D. Dollberg, Ph.D.; J. Palassis; B. A. Lange, Ph.D., NIOSH/DPSE; and C. C. Anderson, SRI International.

Table 1. Absorption correction factor as a function of transmittance for some silica-silver peak combinations.

Transmittance		f(T) (at indicated degrees 2-θ)							
	Silica	26.66	26.66	20.83	20.83	21.93	21.93	21.62	21.62
T	Silver	38.12	44.28	38.12	44.28	38.12	44.28	38.12	44.28
1.00		1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
0.99		1.0071	1.0082	1.0091	1.0105	1.0087	1.0100	1.0088	1.0101
0.98		1.0144	1.0166	1.0184	1.0212	1.0174	1.0201	1.0177	1.0204
0.97		1.0217	1.0251	1.0278	1.0321	1.0264	1.0305	1.0268	1.0309
0.96		1.0292	1.0337	1.0373	1.0432	1.0355	1.0410	1.0360	1.0416
0.95		1.0368	1.0425	1.0470	1.0544	1.0447	1.0517	1.0453	1.0524
0.94		1.0445	1.0514	1.0569	1.0659	1.0541	1.0625	1.0548	1.0635
0.93		1.0523	1.0605	1.0670	1.0776	1.0636	1.0736	1.0645	1.0747
0.92		1.0602	1.0697	1.0772	1.0894	1.0733	1.0849	1.0743	1.0861
0.91		1.0683	1.0791	1.0876	1.1015	1.0831	1.0963	1.0844	1.0977
0.90		1.0765	1.0886	1.0982	1.1138	1.0932	1.1080	1.0945	1.1096
0.89		1.0848	1.0983	1.1089	1.1264	1.1034	1.1199	1.1049	1.1216
0.88		1.0933	1.1081	1.1199	1.1392	1.1137	1.1320	1.1154	1.1339
0.87		1.1019	1.1181	1.1311	1.1522	1.1243	1.1443	1.1261	1.1464
0.86		1.1106	1.1283	1.1424	1.1654	1.1350	1.1568	1.1370	1.1592
0.85		1.1195	1.1387	1.1540	1.1790	1.1460	1.1696	1.1481	1.1722
0.84		1.1286	1.1493	1.1657	1.1927	1.1571	1.1827	1.1595	1.1854
0.83		1.1378	1.1600	1.1777	1.2068	1.1685	1.1959	1.1710	1.1989
0.82		1.1471	1.1709	1.1899	1.2211	1.1800	1.2095	1.1827	1.2126
0.81		1.1566	1.1821	1.2024	1.2357	1.1918	1.2232	1.1946	1.2266
0.80		1.1663	1.1934	1.2150	1.2506	1.2038	1.2373	1.2068	1.2409
0.79		1.1762	1.2050	1.2280	1.2658	1.2160	1.2516	1.2192	1.2555
0.78		1.1863	1.2168	1.2411	1.2812	1.2284	1.2663	1.2319	1.2703
0.77		1.1965	1.2288	1.2546	1.2971	1.2411	1.2812	1.2447	1.2855
0.76		1.2069	1.2410	1.2683	1.3132	1.2540	1.2964	1.2579	1.3009
0.75		1.2175	1.2535	1.2822	1.3297	1.2672	1.3119	1.2713	1.3167
0.74		1.2283	1.2662	1.2965	1.3465	1.2806	1.3278	1.2849	1.3328
0.73		1.2394	1.2792	1.3110	1.3637	1.2944	1.3440	1.2989	1.3493
0.72		1.2506	1.2924	1.3259	1.3812	1.3084	1.3605	1.3131	1.3661
0.71		1.2621	1.3059	1.3410	1.3991	1.3226	1.3774	1.3276	1.3883
0.70		1.2738	1.3197	1.3565	1.4174	1.3372	1.3946	1.3424	1.4008
0.69		1.2857	1.3337	1.3723	1.4362	1.3521	1.4122	1.3576	1.4187
0.68		1.2979	1.3481	1.3885	1.4553	1.3673	1.4303	1.3730	1.4370
0.67		1.3103	1.3628	1.4050	1.4749	1.3829	1.4487	1.3888	1.4558
0.66		1.3230	1.3777	1.4218	1.4949	1.3987	1.4675	1.4050	1.4749
0.65		1.3359	1.3931	1.4390	1.5154	1.4150	1.4868	1.4215	1.4945
0.64		1.3491	1.4087	1.4567	1.5363	1.4316	1.5064	1.4383	1.5145
0.63		1.3626	1.4247	1.4747	1.5578	1.4485	1.5266	1.4556	1.5350
0.62		1.3765	1.4411	1.4931	1.5797	1.4659	1.5472	1.4732	1.5560
0.61		1.3906	1.4578	1.5120	1.6022	1.4836	1.5684	1.4913	1.5775
0.60		1.4050	1.4749	1.5314	1.6252	1.5018	1.5900	1.5098	1.5995

Transmittance		f(T) (at indicated degrees 2-θ)							
T	Silica	26.66	26.66	20.83	20.83	21.93	21.93	21.62	21.62
	Silver	38.12	44.28	38.12	44.28	38.12	44.28	38.12	44.28
0.59		1.4198	1.4925	1.5511	1.6488	1.5204	1.6122	1.5287	1.6221
0.58		1.4349	1.5104	1.5714	1.6730	1.5394	1.6349	1.5481	1.6452
0.57		1.4504	1.5288	1.5922	1.6978	1.5590	1.6582	1.5679	1.6689
0.56		1.4662	1.5476	1.6135	1.7233	1.5790	1.6820	1.5883	1.6932
0.55		1.4824	1.5670	1.6353	1.7494	1.5995	1.7065	1.6092	1.7181
0.54		1.4991	1.6858	1.6577	1.7762	1.6205	1.7317	1.6306	1.7437
0.53		1.5161	1.6071	1.6807	1.8037	1.6421	1.7575	1.6525	1.7699
0.52		1.5336	1.6279	1.7043	1.8319	1.6642	1.7840	1.6751	1.7969
0.51		1.5515	1.6493	1.7285	1.8609	1.6870	1.8112	1.6982	1.8246
0.50		1.5699	1.6713	1.7534	1.8908	1.7103	1.8391	1.7220	1.8531

APPENDIX:

INTERFERENCES

Interferences include micas (muscovite, biotite), potash, feldspars (microcline, plagioclase), montmorillonite, sillimanite, zircon, graphite, iron carbide, clinoferrosillite, wollastonite, sanidine, leucite, orthoclase and lead sulfide.

The patterns for three forms of aluminum phosphate (JCPDS 10-423, 11-500, 20-44) are practically identical to those of quartz, cristobalite and tridymite, respectively. The quartz secondary and cristobalite primary peaks are close; cristobalite secondary peak is overlapped by a quartz peak; tridymite, if present in sufficient quantity, will interfere with all of the main (primary, secondary and tertiary) quartz and cristobalite peaks. Silver chloride, if present on the silver filter, interferes slightly with the primary quartz peak. Many of these interferents occur in the presence of quartz; however, in a study of samples collected in 11 different industries, Altree-Williams [16] found no significant interferences.

The presence of elements such as iron can result in appreciable X-ray fluorescence which leads to high background intensity. A diffracted beam monochromator will minimize this problem.

If calcite is present, loss of quartz will occur when samples are ashed in a muffle furnace. See SAMPLE PREPARATION section for procedure to remove calcite.

If interferences with the primary quartz peak are present, use a different diffraction peak of the silica polymorph with a commensurate decrease in detection limit and precision. When overlaps are not severe, a smaller receiving slit or chromium radiation may be used; however, a new calibration curve will be necessary.

FORMULA: SiO_2

M.W.: 60.08

SILICA, CRYSTALLINE

METHOD: 7601
ISSUED: 2/15/84

OSHA and ACGIH: Quartz (respirable), 10 mg/m³/(% SiO_2 + 2); Cristobalite and Tridymite (respirable), 1/2 the above

NIOSH: 0.05 mg/m³ [1]

PROPERTIES: solid; d 2.65 g/cm³ @ 0 °C; Crystalline transformations: quartz to tridymite @ 867 °C; tridymite to cristobalite @ 1470 °C; α-quartz to β-quartz @ 573 °C

SYNONYMS: free crystalline silica; silicon dioxide; CAS #14808-60-7 (quartz), 14464-46-1 (cristobalite), 15468-32-3 (tridymite).

SAMPLING

SAMPLER: CYCLONE + FILTER (10-mm nylon cyclone + 0.8-µm or 5-µm PVC or MCE membrane)

FLOW RATE: 1.7 L/min

VOL-MIN: 400 L
-MAX: 800 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: required; area respirable or settled dust, 1 to 5 g

ACCURACY

RANGE STUDIED: not studied

BIAS: none known

OVERALL PRECISION (s_r): not measured

MEASUREMENT

TECHNIQUE: VISIBLE ABSORPTION SPECTROPHOTOMETRY

ANALYTE: silicon complexes-silicomolybdate (420 nm) and molybdenum blue (820 nm)

DIGESTION: phosphoric acid, to remove interferring silicon compounds

FILTRATION: to collect undigested material

DISSOLUTION: crystalline silica in HF

CALIBRATION: quartz dissolved in HF

RANGE: silicomolybdate: 0.1 to 2.5 mg SiO_2; molybdenum blue: 0.02 to 0.15 mg SiO_2

ESTIMATED LOD: 10 µg SiO_2

PRECISION (s_r): 0.09 [2]

APPLICABILITY: Determination of crystalline silica in respirable or total dust, settled dust and in biological samples [2,6]. The three crystalline polymorphs cannot be distinguished by this method. The working range is 0.04 to 5 mg/m³ for a 500-L air sample.

INTERFERENCES: Any silicon-containing compound present at the time of dissolution by HF and dissolved by HF will give a positive interference. See APPENDIX A.

OTHER METHODS: This is P&CAM 106 [2]. X-ray diffraction (XRD; Method 7500) can distinguish the three polymorphs and does not detect amorphous silica. Silicates interfere with XRD but are removed by phosphoric acid cleanup. Infrared spectrometry (IR; Method 7602) can determine the three polymorphs, although if two or more are present, a less sensitive peak must be used. Amorphous silica and silicates, in large amounts, interfere with IR.

REAGENTS:

1. Quartz* (NBS SRM # 1878 or Min-U-Sil 5 (quartz), Pennsylvania Glass Sand Co., Berkley Springs, WV).
2. Hydrofluoric acid, 48% (HF).*
3. Orthophosphoric acid, 85% H_3PO_4.*
4. Silica-free water. All water used must be deionized and stored in polyethylene containers.
5. Hydrochloric acid (HCl),* 1:10 v/v conc. HCl in deionized water.
6. Sulfuric acid, 10 N.* Cautiously add 555 mL conc. H_2SO_4 to about 1.3 L of deionized water. Cool. Dilute to 2 L.
7. Nitric acid, conc.*
8. Perchloric acid, conc. Use only if samples have been collected on PVC filters.
9. Boric acid solution, 5%. 200 g boric acid crystals in 4 L warm deionized water. Cool. Filter with vacuum through a 0.45-µm membrane filter. Store in a polyethylene container.
10. Molybdate reagent. Dissolve 50 g ammonium molybdate tetrahydrate in about 400 mL deionized water. Add 50 mL conc. sulfuric acid. Cool. Dilute to 500 mL. Store in dark.
11. Reducing solution. Dissolve 9 g sodium bisulfite in 80 mL deionized water. In 10 mL deionized water, dissolve 0.7 g anhydrous sodium sulfite and 0.15 g 1-amino-2-naphthol-4-sulfonic acid, in that order. Combine these solutions and dilute to 100 mL with deionized water. Stable ca.one month if stored in refrigerator.
12. Silica stock standard, 0.5 mg/mL. Dissolve 250 mg quartz in 10 mL 48% HF. Dilute to 500 mL with silica-free water. Store in a polyethylene container. Stable indefinitely.

*See Special Precautions.

EQUIPMENT:

1. Personal sampler: 10-mm nylon cyclone (for respirable samples only); polyvinyl chloride (PVC) or mixed cellulose ester (MCE) membrane filters, 37-mm diameter, 5- or 0.8-µm pore size; two-piece filter cassette.
   NOTE: If PVC filters are used, a perchloric acid fume hood, low temperature radio-frequency plasma asher or muffle furnace will be needed to ash them.
2. Personal sampling pump, 1.7 L/min, with flexible connecting tubing.
3. High-volume sampler: 0.5 inch HASL cyclone; PVC or MCE membrane filters, 37-mm diameter, 5- or 0.8-µm pore size, two-piece filter cassette, with high-volume pump, 9 L/min.
4. Precision heater, 550-watt, 115-V, Type RH; 750 watt variable transformer with built-in voltmeter; variable speed rotator, about 30 to 80 rpm range (can be achieved with a variable transformer).
5. Stopwatch or laboratory timer.
6. Phillips beakers, borosilicate glass, 250-mL; short-stemmed glass funnels with bent stems (must be done by laboratory); crucible tongs with tygon or rubber-padded tips; polyethylene stirring rods; polyethylene 50-mm discs.
7. MCE membrane filters, 0.45-µm pore size, 47-mm diameter; filter funnel, including membrane mount and flask assembly, 47-mm.
8. Buret, polypropylene, 10-mL; polyethylene reagent bottles for water, boric acid, and standard solutions.
9. Constant temperature bath, 40 °C.
10. Spectrophotometer, at 420 to 820 nm and 1-cm cuvettes.
11. Hotplate, 150 °C surface temperature.
12. Graduated cylinder or graduated pipet, 10- and 25-mL.
13. Polyethylene graduated cylinder or pipets, 25- and 50-mL.

SPECIAL PRECAUTIONS: Avoid inhaling silica dust [1].

Use personal protective equipment to prevent contact of HF with the skin. HF dissolves glass; use plastic labware for all solutions containing HF. Concentrated acids are corrosive; use appropriate personal protective equipment.

SAMPLING:

1. Calibrate each personal sampling pump to 1.7 L/min with a representative sampler in line.
2. Sample at 1.7 $\pm$ 5% L/min for a total sample size of 499 to 800 L. Do not exceed 2 mg dust loading on the filter.
   NOTE: Do not allow the sampler assembly to be inverted at any time when using a cyclone. Turning the cyclone to anything more than a horizontal orientation may deposit oversized material from the cyclone body onto the filter.

SAMPLE PREPARATION:

   NOTE: Successful use of this method depends on close attention to details and uniformity in sample handling procedures.
3. Place a weighed bulk sample containing no more than 2.5 mg SiO_2, or a membrane filter sample, in a 250-mL Phillips beaker. Add 3 to 4 mL conc. HNO_3 to ash MCE membrane filters. Heat on a hotplate to absence of brown fumes.
4. Add an additional 2 mL conc. HNO_3 and heat to dryness. Repeat this step until any remaining residue is white.
   NOTE: Ash PVC filters using 2 mL conc. $HClO_4$. Heat slowly until the filter shrinks, turns brown and is dissolved. Add additional portions of $HClO_4$ if necessary. If a perchloric acid hood is not available, see APPENDIX B for alternate ashing procedures for PVC filters. Pretreatment procedures to remove various contaminants from bulk samples are outlined in reference [5].
5. Add 25 mL 85% H_3PO_4 to the beaker. Cover the beaker with a bent-stem funnel. Make sure that the tip of the funnel stem touches the wall of the flask. Start reagent blanks at this time.
   NOTE: The bent-stem funnel is used to prevent too rapid dehydration of the sample and to prevent spattering.
6. Place the 550-watt heater on the rotator in a fume hood. Preheat the 550-watt heater at 70 V for at least 45 min. Heat each sample and blank for exactly 8 min, swirling it by the action of the variable speed rotator.
   NOTE: The solution in the flask should reach 240 °C during this procedure.
7. Remove the beaker from the heater with padded tongs and swirl it for 1 min. Allow the beaker to cool. Add about 125 mL warm (60 to 70 °C) deionized water and swirl to mix completely.
8. Filter the sample with suction through a 47-mm filter. Wash thoroughly with 1:10 HCl.
9. Place the 47-mm filter in the bottom of a 150-mL polyethylene beaker. Add 0.5 mL 48% HF to the filter surface. Float a thin polyethylene disc of about 50 mm diameter over the 47-mm filter and cover the beaker. Allow to stand for 30 min.

CALIBRATION AND QUALITY CONTROL:

10. Prepare a calibration graph for the silico-molybdate range by diluting, e.g., 1-, 2-, 3-, 4-, 5- and 6-mL aliquots of the silica stock standard to 25 mL with silica-free water in polyethylene beakers and following the measurement procedure (steps 14 through 16). Plot absorbance vs. mg SiO_2.
11. Prepare a calibration graph in the molybdenum blue range by diluting the working standards in step 10 1:25, and carrying the resulting standard solutions through steps 14 through 16. Plot absorbance vs. mg SiO_2.
12. Prepare control samples containing a silicate compound (about 50 mg $MgSiO_4$ sample) in addition to the quartz. Recovery of quartz is low and precision is much worse if quartz only is present during the phosphoric acid treatment.

MEASUREMENT:

13. Add 25 mL silica-free water.
14. Add 50 mL boric acid solution. Stir well. Cover. Heat the solution in a 40 °C waterbath for 10 min.
15. Add 4 mL molybdate reagent while stirring, staggering the addition at 2-min intervals between samples. Time from the beginning of the addition of molybdic acid. Wait 20 min, then add 20 mL 10 N H_2SO_4 and stir thoroughly.
16. Note the color of the solution.
    a. If any yellow persists, read within 2 min after acidification in a spectrophotometer at 420 nm against deionized water.
    b. If a colorless solution results, allow it to stand for 2 to 5 min and add 1 mL 1-amino-2-naphthol-4-sulfonic acid reagent. Mix and read after 20 min at 820 nm against deionized water. This color is stable for several hours.

    Record the absorbances of the sample, A, and reagent blank, B.

CALCULATIONS:

17. Calculate the concentration of crystalline silica, C (mg/m^3), in the air volume sampled, V (L), using the slope, m (μg^{-1}) of the appropriate calibration graph:

$$C = \frac{(A - B)}{m \cdot V}.$$

EVALUATION OF METHOD:

This method is based on the well-characterized Talvitie method [2,3,4].

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Crystalline Silica, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 75-120 (1974).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 106, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[3] Talvitie, N. A. Determination of Free Silica: Gravimetric and Spectrophotometric Procedures Applicable to Airborne and Settled Dust, Am. Ind. Hyg. Assoc. J., 25, 169-178 (1964).
[4] Talvitie, N. A. Determination of Quartz in Presence of Silicates Using Phosphoric Acid, Anal. Chem., 23(4), 623-626 (1951).

[5] Talvitie, N. A. and Frances Hyslop. Colorimetric Determination of Siliceous Atmospheric Contaminants, Am. Ind. Hyg. Assoc. J., 19(1), 54-58 (1958).
[6] Sweet, D. V., F. R. Wolowicz, and J. V. Crable. Spectrophotometric Determination of Free Silica, Am. Ind. Hyg. Assoc. J., 34, 500-506 (1973).

METHOD WRITTEN BY: Michele Bolyard, CIH, and Jensen Groff, NIOSH/DPSE, and Doris Sweet, NIOSH/DSDTT.

APPENDIX A:

INTERFERENCES

Some silicates may be resistant to phosphoric acid digestion [4]. Any silicates not removed by the phosphoric acid treatment will give a positive interference. Amorphous silica, if not completely removed by phosphoric acid treatment, will give a positive interference. Phosphate ion complexes molybdic acid to produce a yellow phosphomolybdate color which is dissipated by lowering the pH of the solution with 10 N sulfuric acid. Excess ferric ion (more than 1 mg) will consume the reducing agent and inhibit the reduction of silicomolybdate to molybdenum blue. If more than 1 mg ferric ion is present, it should be removed by pretreatment with 10:1 $HCl:HNO_3$.

APPENDIX B:

ALTERNATE ASHING PROCEDURES FOR PVC FILTERS

If a perchloric acid fume hood is unavailable, ash PVC filters with one of the following methods.

1. Muffle furnace ashing: Wash the filters with 25% v/v HCl if the samples contain a significant amount of calcite (20% of the total dust loading); otherwise, proceed to next paragraph. Place a 0.5-µm, 37-mm PVC filter in the filtration apparatus. Center the sample filter on top of the first filter. Clamp the filter funnel over the frit so that the dust deposit is completely exposed. Add 10 mL HCl solution and 5 mL 2-propanol to the filter funnel; allow to sit for 5 min. Apply vacuum to aspirate the acid/alcohol solution from the filter. Wash with three 10-mL portions of deionized water. Release the vacuum.

   Place the filter samples in porcelain crucibles, cover loosely and ash in a muffle furnace for 2 hrs at 600 °C (800 °C if graphite is present). Add several mL of 2-propanol to the ash, scrape the crucible to loosen all particles and transfer the residue to a 250-mL borosilicate glass Phillips beaker. Wash crucible several times and add wash to the beaker. Heat on a sparkless hotplate to evaporate the 2-propanol. When beaker is dry, proceed with step 4 of sample preparation.

2. Low temperature ashing: Place the filters in 50-mL glass beakers within the LTA so that the sample exposure to the plasma is optimized. Ash according to manufacturer's instructions. After ashing, add 2-propanol to the beaker to transfer the residue to a 250-mL borosilicate Phillips beaker. Wash the beaker with 2-propanol several times, adding the washings to the Phillips beaker. Heat on a sparkless hotplate to remove the 2-propanol. When the beaker is dry, proceed to step 4 of sample preparation.

FORMULA: SiO_2

M.W.: 60.08

SILICA, CRYSTALLINE (IR)

METHOD: 7602
ISSUED: 2/15/84

OSHA: Quartz (respirable); 10 mg/m³/(% SiO_2 + 2); Cristobalite and Tridymite (respirable); 1/2 the above
&
ACGIH:
NIOSH: 0.05 mg/m³ [1]

PROPERTIES: solid; d 2.65 g/cm³ @ 0 °C; Crystalline transformations: quartz to tridymite @ 867 °C; tridymite to cristobalite @ 1470 °C; α-quartz to β-quartz @ 573 °C

SYNONYMS: free crystalline silica; silicon dioxide; CAS #14808-60-7 (quartz), CAS #14464-46-1 (cristobalite), CAS #15468-32-3 (tridymite).

SAMPLING

SAMPLER: CYCLONE + FILTER (10-mm nylon cyclone + 0.8-µm or 5-µm PVC or MCE membrane)

FLOW RATE: 1.7 L/min

VOL-MIN: 400 L
-MAX: 800 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: required; area respirable or settled dust

ACCURACY

RANGE STUDIED: not studied

BIAS: none known

OVERALL PRECISION (s_r): not measured

MEASUREMENT

TECHNIQUE: INFRARED ABSORPTION SPECTROPHOTOMETRY

ANALYTE: quartz

ASH: muffle furnace or RF plasma asher

PELLET: mix residue with KBr; press 13 mm pellet

IR: scan absorbance from 1000 to 600 cm^{-1}

CALIBRATION: quartz diluted in KBr

RANGE: 10 to 160 µg quartz

ESTIMATED LOD: 5 µg quartz

PRECISION (s_r): <0.15 @ 30 µg quartz per sample, in coal dust [2]

APPLICABILITY: The working range is 0.025 to 0.4 mg/m³ for a 400-L air sample. Cristobalite and tridymite also have major absorbance peaks at 800 cm^{-1} which can be used for their determination [2-7].

INTERFERENCES: Amorphous silica, calcite, cristobalite, kaolinite and tridymite interfere; see APPENDIX.

OTHER METHODS: This is P&CAM 110 [2]. Crystalline silica can also be determined by X-ray diffraction (Method 7500) and spectrophotometry (Method 7601). XRD can distinguish the three polymorphs and does not detect amorphous silica. Silicates, which interfere with XRD, are removed by phosphoric acid cleanup.

419 Preceding page blank

REAGENTS:

1. Quartz* (NBS SRM # 1878 or Min-U-Sil 5 [quartz, Pennsylvania Glass Sand Co., Berkley Springs, WV).
2. Potassium bromide (KBr), infrared quality.
3. Ethanol, 95% for cleaning sample handling equipment.*
4. Hydrochloric acid, 9% w/w. Dilute 25 mL conc. HCl (37% w/w) to 100 mL with deionized water.
5. Calibration stock standard, 0.5% w/w. Accurately weigh and thoroughly mix 5 g KBr (dried overnight at 110 °C) with 25 mg quartz. Store in a bottle in a desiccator.

*See Special Precautions.

EQUIPMENT:

1. Sampler: 10-mm nylon cyclone; polyvinyl chloride (PVC) or mixed cellulose ester (MCE) membrane filters, 37-mm diameter, 0.8- or 5-µm pore size; two-piece filter cassette.
2. Personal sampling pump, 1.7 L/min, with flexible connecting tubing.
3. High-volume sampler: 0.5-inch HASL cyclone; PVC or MCE membrane filters, 37-mm diameter, 0.8- or 5-µm pore size; two-piece filter cassette, with high-volume pump, 9 L/min.
4. Infrared spectrophotometer; laboratory press for preparing KBr pellets; 13-mm KBr pellet die (evacuable).
5. Low temperature (RF Plasma) asher and aluminum weighing pans or muffle furnace and porcelain crucibles.
6. 50 mm agate or mullite mortar and pestle; metal microspatula; non-serrate, non-magnetic forceps; desiccator, camel's hair brush, glassine paper.
7. Analytical balance (0.01 mg) for preparing standards.
8. Membrane filtration apparatus, 37-mm.

SPECIAL PRECAUTIONS: Avoid inhaling silica dust [1].

Ethanol is flammable; keep away from flames.

SAMPLING:

1. Calibrate each personal sampling pump to 1.7 L/min with a representative sampler in line.
2. Sample at 1.7 L/min for a total sample size of 400 to 800 L. Do not exceed 2 mg total dust loading on the filter.

   NOTE: Do not allow the sampler assembly to be inverted at any time when using a cyclone. Turning the cyclone to anything more than a horizontal orientation may deposit oversized material from the cyclone body onto the filter.

SAMPLE PREPARATION:

3. Use one of the following methods to ash samples and blanks:
   a. Low temperature (RF Plasma) ashing: Place the filters in labelled aluminum dishes (previously rinsed with distilled water followed by ethanol and air dried). Place the dishes within the low temperature asher so that sample exposure to the plasma is optimized. Ash according to manufacturer's instructions. Carefully bring asher to atmospheric pressure and remove the dishes.
   b. Muffle furnace ashing: Wash the filters with 9% w/w hydrochloric acid if the samples contain a significant amount of calcite (greater than 20% of the total dust loading); otherwise, proceed to the next paragraph. Place a 0.5-µm, 47-mm PVC filter in the filtration apparatus. Remove the sample filter from the cassette and center it on top of the first filter. Clamp the fiter funnel over the frit so that the dust deposit is

completely exposed. Add 10 mL 9% w/w HCl and 5 mL 2-propanol to the filter funnel; allow to sit for 5 min. Apply vacuum and slowly aspirate the acid and alcohol in the funnel, washing with three successive 10-mL portions of distilled water. Release the vacuum. Place the filter samples in porcelain crucibles, loosely cover, and ash in muffle furnace for 2 hrs at 600 °C (800 °C if graphite is present).

4. Add approximately 300 mg KBr, dried overnight at 110 °C, weighed to 0.1 mg, directly to each sample. Mix the sample ash and KBr thoroughly with a pestle. Transfer to mortar to complete mixing if necessary. Transfer the mixture to a 13-mm evacuable pellet die using glassine paper and camel's hair brush. Press a pellet using standard technique. Weigh the finished pellet to 0.1 mg. Calculate the ratio (weight of finished pellet ÷ weight KBr initially added); it is usually about 0.98. Clean sample handling equipment with ethanol between samples.
NOTE: A low relative humidity environment will facilitate sample handling when using KBr.

CALIBRATION AND QUALITY CONTROL:

5. Prepare working standard pellets:
   a. Weigh, to 0.001 mg, portions of calibration stock standard containing 10 to 200 µg quartz.
   b. Add an accurately-weighed 300 mg KBr. Proceed as in step 4.
   c. Calculate the ratio (weight of finished pellet/weight of solids added); usually about 0.98.
   d. Determine the absorbance at 800 cm^{-1} for each standard pellet following the analytical procedure (step 8). Plot absorbances vs. µg SiO_2.
6. If samples were low temperature ashed (step 3.a) and kaolinite is present, prepare pellets containing 100 to 600 µg kaolinite. Determine the abosrbance at 800 cm^{-1} and at 915 cm^{-1} (steps 8 and 9). Plot absorbance at 915 cm^{-1} as ordinate vs. absorbance at 800 cm^{-1} as abscissa. Prepare at least five different kaolinite concentrations. Use this curve to correct the abosrbance value at 800 cm^{-1} for any sample containing kaolinite.
7. Carry media blanks and filters spiked with known amounts of quartz through the sample preparation procedures (steps 3 and 4) to monitor for contamination and losses.

MEASUREMENT:

8. Set the infrared spectrophotometer to absorbance mode and to the appropriate settings for quantitative analysis. Scan the pellet from 1000 cm^{-1} to 600 cm^{-1}. Rotate the pellet 45° and scan this diameter. Repeat twice more until 4 scans have been obtained. If the peak at 800 cm^{-1} is small, use 5X ordinate expansion to enhance the peak height. Draw an appropriate baseline under the absorbance band at 800 cm^{-1} from approximately 820 to 670 cm^{-1}. Measure the absorbance at 800 cm^{-1} from maximum to baseline in absorbance units. Average the four values for each sample.
9. If the sample was ashed at low temperature (step 3.a), the presence of kaolinite will be indicated by an absorption band with a maximum at 915 cm^{-1}. Draw an appropriate baseline under this band from approximately 960 to 860 cm^{-1} and measure the absorbance at 915 cm^{-1} from this baseline to the maximum.

CALCULATIONS:

10. Correction for kaolinite. Determine the sample absorbance at 915 cm^{-1} (step 9), refer to the kaolinite curve (step 6) to find the absorbance at 800 cm^{-1} due to kaolinite. Subtract this amount from the sample absorbance at 800 cm^{-1}. Use this corrected value in step 11.

11. If correction for kaolinite is not required, use the absorbance at 800 cm^{-1} to find the weight of quartz, w (µg), from the calibration graph.
12. Calculate the concentration of silica, C (mg/m^3), in the volume of air sampled, V (L):

$$C = \frac{w}{V} .$$

13. If percent quartz, % Q, is required, divide the w by the total sample weight, W (mg):

$$\% Q = \frac{w}{W} \cdot 10^{-1} .$$

EVALUATION OF METHOD:
This method is based on the well-characterized infrared method [2].

REFERENCES:
[1] Criteria for a Recommended Standard...Occupational Exposure to Crystalline Silica, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 75-120 (1974).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 110, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[3] Larsen, D. J., L. J. von Loenhoff and J. V. Crable. The Quantitative Determination of Quartz in Doal Dust by Infrared Spectroscopy, Am. Ind. Hyg. Assoc. J., 33; 367-372 (1972).
[4] Dodgson, J. and W. Whittaker. The Determination of Quartz in Respirable Dust Samples by Infrared Spectrophotometry-1: The Potassium Bromide Disc Method, Ann. Occup. Hyg., 16; 373-387 (1973).
[5] Cares, J. W., A. S. Goldin, J. J. Lynch and W. A. Burgess. The Determination of Quartz in Airborne Respirable Granite Dust by Infrared Spectrophotometry, Am. Ind. Hyg. Assoc. J., 34; 298-305 (1973).
[6] Taylor, D. G., C. M. Nenadic and J. V. Crable. Infrared Spectra for Mineral Identification, Am. Ind. Hyg. Assoc. J., 31, 100-108 (1970).
[7] Talvitie, N. A. Determination of Quartz in the Presence of Silicates Using Phosphoric Acid, Anal. Chem., 23, 623-626 (1951).

METHOD REVISED BY: Michele Bolyard, CIH, NIOSH/DPSE.

APPENDIX:

INTERFERENCES
Quartz and cristobalite can be determined in each other's presence by the use of less sensitive bands at 695 cm^{-1} (quartz) and 625 cm^{-1} (cristobalite). Tridymite can only be determined in the absence of the other two polymorphs; it is rarely encountered in industrial hygiene samples. Interfering silicates can be removed using a phosphoric acid cleanup procedure [7].

Cristobalite and tridymite interfere positively at the 800 cm^{-1} peak, although they are rarely present in industrial hygiene samples. Kaolinite, a common component of coal, can interfere when RF plasma ashing is used to remove the collection filter, if it is present in sufficient quantity. A correction procedure is outlined in the method (steps 6 and 10). Calcite, at greater than 20% of the total dust loadings, can interfere by reacting with the quartz during muffle ashing. A procedure for its removal is given (step 3.b). Amorphous silica may interfere if present in large amounts. This interference can be minimized by accounting for its broad absorbance band when drawing the baseline.

FORMULA: $[(CH_3CH_2O)_2PO]_2O$; $C_8H_{20}O_7P_2$

M.W.: 290.19

TETRAETHYL PYROPHOSPHATE

METHOD: 2504
ISSUED: 2/15/84

OSHA: 0.004 ppm (skin)
NIOSH: Group I Pesticide [1]
ACGIH: 0.05 mg/m³ (skin); 0.2 mg/m³ STEL
(1 ppm = 11.86 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.185 g/mL @ 20 °C;
BP 124 °C @ 1mm Hg; MP 32 °C;
VP 0.063 Pa (0.00047 mm Hg;
0.62 ppm); @ 30 °C

SYNONYMS: tetraethyl pyrophosphate; diphosphoric acid tetraethyl ester; pyrophosphoric acid tetraethyl ester; CAS #107-49-3.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(2 Chromosorb 102 tubes in series,
100 mg and 50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 3 L
-MAX: 48 L

SHIPMENT: routine

SAMPLE STABILITY: at least 8 days @ 25 °C [2]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.025 to 0.102 mg/m³ [2]
(48-L samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.086 [2]

MEASUREMENT

!
!TECHNIQUE: GAS CHROMATOGRAPHY, FPD
!
!ANALYTE: TEPP
!
!DESORPTION: 1 mL toluene; stand 60 min
!
!INJECTION VOLUME: 5 µL
!
!TEMPERATURE-INJECTION: 200 °C
! -DETECTOR: 200 °C
! -COLUMN: 115 °C
!
!CARRIER GAS: N_2 or He, 30 mL/min
!
!COLUMN: 2 m x 2 mm ID glass; Super-Pak 20M
!
!CALIBRATION: TEPP in toluene
!
!RANGE: 1 to 6 µg per sample [2]
!
!ESTIMATED LOD: 0.1 µg per sample [2]
!
!PRECISION (s_r): 0.039 [2]
!
!

APPLICABILITY: The working range is 0.025 to 0.15 mg/m³ for a 40-L air sample. The method is useful for both area and personal samples. The method can measure a STEL of 0.33 mg/m³.

INTERFERENCES: None identified.

OTHER METHODS: This is P&CAM 336 [3] in a revised format.

REAGENTS:

1. TEPP, purified*.
   NOTE: TEPP is hygroscopic and easily hydrolized.
2. Tripropyl phosphate, reagent grade, or other suitable internal standard.
3. Toluene, reagent grade.
4. Eluent: Dilute a weighed amount of tripropyl phosphate to 100 mL with toluene. Concentration of solution must be within the linear range of the FPD.
5. Extracted resin. Chromosorb 102 20/40 mesh (Johns Manville Corp.) or equivalent extracted in Soxhlet apparatus with 1:1 methanol:acetone solution for 2 hrs and dried at 115 °C under vacuum for 1 hr.
6. Nitrogen, purified.
7. Hydrogen, prepurified.
8. Air, filtered.
9. Calibration stock solution, 1.18 mg/mL. Dilute 11.8 mg (10 µL) TEPP to 10 mL with eluent. Prepare in duplicate.

*See Special Precautions.

EQUIPMENT:

1. Sampler: two glass tubes, 10-cm long, 8-mm OD, 6-mm ID, flame-sealed ends, front tube containing a 100-mg section of extracted resin and a back containing a 50-mg section, retained by silylated glass wool plugs in each tube. Pressure drop across the tubes in series at 1 L/min airflow must be less than 3.4 kPa.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame photometric detector, phosphorus filter, integrator and column (page 2504-1).
4. Vials, 2-mL, PTFE-lined caps.
5. Syringe, volumetric, 10- and 100-µL.
6. Flasks, volumetric, 10-mL.
7. Pipettes, volumetric, 1-mL, with pipet bulb.
8. File.

SPECIAL PRECAUTIONS: TEPP is a cholinesterase inhibitor and can be absorbed through the skin. Wear protective gloves and suitable protective clothing when handling the pure material [1].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Connect the two sorbent tubes with a short piece of flexible tubing. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 3 to 48 L.
4. Separate the front and backup tubes. Cap the tubes with plastic (not rubber) caps. This prevents migration of TEPP between sorbent sections. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 60 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.1 to 6 µg TEPP per sample.
   a. Add known amounts of calibration stock solution to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. µg TEPP).
9. Determine desorption efficiency (DE) at least once for each batch of Chromosorb 102 used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. µg TEPP recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2504-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE) of TEPP found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of TEPP in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method P&CAM 336 [3] was evaluated over the range 0.025 to 0.102 mg/m³ at 21.5 °C and 735.3 mm Hg using 48-L samples [2,4]. Overall precision, s_r, was 0.086 with an average recovery of 99.4%, representing a non-significant bias. The concentration of TEPP was independently verified by sampling the generator with toluene-filled bubblers and analysis by GC/FPD. Desorption efficiency averaged 0.994 in the range 1.1 µg to 4.8 µg per sample. After sampling an atmosphere containing 0.41 µg/m³ at 0.18 L/min at 90% RH for 300 min, only 0.2% of the influent concentration was detected breaking through the sorbent bed. This did not constitute breakthrough as it is defined (effluent concentration from sorbent bed is 5% of influent concentration) [2].

REFERENCES:
[1] Criteria for a Recommended Standard...Occupational Exposure During the Manufacture and Formulation of Pesticides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-174 (1978).
[2] Backup Data Report S305, TEPP, prepared under NIOSH Contract No. 210-76-0123 (August, 1979).
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 6, P&CAM 336, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).
[4] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY: Eugene R. Kennedy, Ph.D., NIOSH/DPSE; P&CAM 336 originally developed under NIOSH Contract No. 210-76-0123.

FORMULA: $(CH_3)_2NCSSCN(CH_3)_2$;
$C_6H_{12}N_2S_4$
M.W.: 240.43

THIRAM

METHOD: 5005
ISSUED: 2/15/84

OSHA: 5 mg/m³
NIOSH: Group I Pesticide [1]; suspect carcinogen
ACGIH: 5 mg/m³; STEL 10 mg/m³

PROPERTIES: white crystalline powder; d 1.29 g/mL; MP 155 °C; VP not significant

SYNONYMS: bis(dimethylthiocarbamoyl)disulfide; tetramethylthiuram disulfide; tetramethylthioperoxydicarbonic diamide; CAS# 137-26-8.

SAMPLING

SAMPLER: FILTER
(1-µm PTFE membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 10 L
-MAX: 400 L

SHIPMENT: routine

SAMPLE STABILITY: 1 week

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: desirable; 1 to 5g

ACCURACY

RANGE STUDIED: 3 to 12 mg/m³ [2]
(240-L sample)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.055 [2]

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: Thiram

EXTRACTION: (filter) 10 mL CH_3CN, 30 min;
(cassette top) 10 mL CH_3CN rinse

INJECTION VOLUME: 5 µL

MOBILE PHASE: 60% acetonitrile/40% water, 1 mL/min

DETECTOR: UV @ 254 nm; 1-cm cell

COLUMN: µ-Bondapak C_{18} (30 cm x 3.9 mm ID stainless steel); ambient temperature

CALIBRATION: solutions of Thiram in acetonitrile

RANGE: 0.1 to 3 mg per sample [2]

ESTIMATED LOD: 0.005 mg per sample [2]

PRECISION (s_r): 0.012 [2]

APPLICABILITY: The working range is 0.5 to 15 mg/m³ for a 200-L air sample. NIOSH has used this method at facilities using Thiram as an insecticide.

INTERFERENCES: None known.

OTHER METHODS: This is Method S256 [3] in a revised format. An earlier spectrophotometric method, P&CAM 228 [4], has not been revised because of excessive analytical variability [5].

REAGENTS:

1. Acetonitrile, HPLC grade.*
2. Water, distilled, deionized.
3. Thiram, reagent grade.*
4. Air or nitrogen, compressed for drying syringes.
5. Calibration stock solution, 0.75 mg/mL. Dissolve an accurately weighed 7.5 mg Thiram in acetonitrile and dilute to 10 mL. Prepare fresh daily in duplicate.

*See Special Precautions.

EQUIPMENT:

1. Sampler: 1-µm PTFE membrane filter (Millipore FA or equivalent), 37-mm diameter, two-piece polystyrene cassette filter holder with backup pad, sealed with tape or a shrinkable band. Filter holders made of Tenite should not be used.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Liquid chromatograph, UV detector at 254 nm, integrator and column (page 5005-1).
4. 13 mm x 5 µm PTFE filters and stainless steel filter holder to protect the LC column.
5. Vials, 20-mL, glass, PTFE-lined screw caps.
6. Syringe, 1-mL, with Luer-Lok fitting.
7. Pipets, 10-mL, with pipet bulb.
8. Tweezers.
9. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Acetonitrile is toxic and flammable; work with it only in a hood.

Thiram is an irritant of skin and mucous membranes and a skin sensitizer and suspected teratogen [1].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at 1 to 3 L/min for a total sample size of 10 to 400 L. Do not exceed 2 mg total dust loading on the filter.
3. Collect a bulk sample (1 to 5 g) in a glass vial with PTFE-lined cap; ship separately from filters.

SAMPLE PREPARATION:

4. Remove filter from cassette with tweezers and place in 20-mL vial.
5. Add 10 mL acetonitrile. Cap the vial.
6. Rinse the inside top of cassette with 10 mL acetonitrile into a 20-mL vial. Cap the vial.
7. Agitate samples during the 30-min desorption period.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.005 to 3 mg Thiram per sample.
   a. Add known amounts of calibration stock solution to acetonitrile in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 9 and 10).
   c. Prepare calibration graph (peak area vs. mg Thiram).

MEASUREMENT:

9. Set liquid chromatograph to conditions on page 5005-1. Inject 10-µL sample aliquot. Rinse and dry syringe between injections.
10. Measure peak area.

CALCULATIONS:

11. Read the mass, mg, of Thiram found in the sample filter (W_f) and top rinse (W_t) and in the average media blank (B) from calibration graph.
12. Calculate the concentration of Thiram, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{(W_f + W_t - B) \cdot 10^3}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method S256 was issued on June 8, 1979 [3], and validated by collecting 18 samples (six each at one-half, one and two times the OSHA standard) from dynamically-generated test atmospheres using Thiram 65 (65% Thiram; Mayer Chemical Co.), as well as a set of six samples which was stored at room temperature for seven days to establish stability [2,5]. The stored sample results were within 2.1% of samples analyzed after one day, indicating adequate storage stability for seven days. Eighteen more samples were spiked directly (six each at one-half, one and two times the OSHA standard). The pooled relative standard deviation for these three sets of samples was found to be 0.012. The average recovery for all three levels was 99.8%; therefore, there is no bias for this method. The pooled relative standard deviation for the three sets of samples collected from test atmospheres was 0.022. Test atmospheres at 12 mg/m^3 Thiram were sampled with PTFE filters followed by bubblers containing acetonitrile; no detectable Thiram (LOD = 0.005 mg) was found in the bubblers indicating that vapor pressure of Thiram was insignificant.

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure During Manufacture and Formulation of Pesticides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-174 (1978).
[2] Backup Data Report S256, NIOSH Contract 210-76-0123, available as Order No. PB 81-244634 from NTIS, Springfield, VA 22161.
[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 5, S256, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[4] Ibid, V. 1, P&CAM 228, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[5] Failure Report S256, NIOSH Contract CDC-99-74-45 (unpublished, 1976).
[6] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY: Y. T. Gagnon, NIOSH/DPSE; S256 originally validated under NIOSH Contract 210-76-0123.

FORMULA: W

M.W.: 183.85

TUNGSTEN (SOLUBLE/INSOLUBLE)

METHOD: 7074
ISSUED: 2/15/84

OSHA: no standard
NIOSH: 1 mg/m³ solubles;
5 mg/m³ insolubles [1]
ACGIH: 1 mg/m³ solubles; 5 mg/m³ insolubles

PROPERTIES: brittle metal; MP 3410 °C;
valence 2,3,4,5,6

SYNONYMS: wolfram; CAS #7440-33-7.

SAMPLING

SAMPLER: FILTER
(0.8-µm cellulose ester membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 170 L @ 1 mg/m³
-MAX: 800 L

SHIPMENT: routine

SAMPLE STABILITY: stable at least 2 weeks @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.42 to 2.0 mg/m³ (soluble) [2];
0.84 to 19.7 mg/m³ (insoluble) [2]

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.055 (soluble) [2];
0.056 (insoluble) [2]

MEASUREMENT

!TECHNIQUE: ATOMIC ABSORPTION, FLAME

!ANALYTE: tungsten

!EXTRACTION: H_2O, 6 min, 25 °C

!ASHING: 1:1 HF:HNO_3, 10 mL; 6 hrs, 150 °C

!FINAL SOLUTION: 0.05 M NaOH/2% Na_2SO_4; 25 mL

!FLAME: nitrous oxide-acetylene, reducing

!WAVELENGTH: 255.1 nm

!BACKGROUND CORRECTION: none used

!CALIBRATION: W in 0.05 M NaOH and 2% Na_2SO_4

!RANGE: 0.1 to 0.5 mg per sample (soluble);
! 0.25 to 12 mg per sample (insoluble)

!ESTIMATED LOD: 25 µg per sample

!PRECISION (s_r): 0.029 [2]

APPLICABILITY: The working range of this method is 0.42 to 2.0 mg/m³ (soluble) and 0.84 to 19.7 mg/m³ (insoluble) for a 400-L air sample. This is an elemental analysis and not compound specific. For cemented tungsten carbide samples, cobalt can be quantitatively determined from the HCl extract.

INTERFERENCES: None known. Ni, Mo, V, Mn, Cr, Co and Fe do not interfere at concentrations up to 50 times the tungsten concentration [3].

OTHER METHODS: This is Method P&CAM 271 [3] in a new format. Method 7300 (ICP-AES) is an alternate measurement method; however, the extraction and ashing procedures described in this method must be followed.

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REAGENTS:

1. Nitric acid, conc. (68 to 71% w/w).
2. Hydrofluoric acid, conc. (49% w/w).*
3. Hydrochloric acid, conc. (38% w/w).
4. Hydrochloric acid, 1% (w/w). Add 26.5 mL conc. HCl to 500 mL water; dilute to 1 L.
5. Sodium hydroxide, 0.5 M. Dissolve 20 g NaOH in 500 mL water; dilute to 1 L.
6. Sodium sulfate, 20% (w/v). Dissolve 20 g Na_2SO_4 in 80 mL water; dilute to 100 mL.
7. Calibration stock solution, 10 mg W/mL. Commercially available or dissolve 1.5985 g Na_2WO_4 (dried at 125 °C) in water; add 10 mL 0.5 M NaOH and dilute to 100 mL.

*See Special Precautions.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-µm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with a nitrous oxide-acetylene burner head.
4. Tungsten hollow cathode lamp.
5. Two-stage regulator for N_2O and acetylene.
6. Beakers, PTFE, 100-mL (with covers).*
7. Volumetric flasks, 10-, 25- and 100-mL.*
8. Assorted volumetric pipettes, as needed, with pipet bulb.*
9. Hotplate for use at 150 °C.
10. Steambath or 100 °C hotplate.
11. Filtering apparatus (funnel, clamp, frit, holder) with 47-mm, 0.45 µm pore size cellulose ester membrane filter.

*Clean all labware conc. nitric with acid and rinse thoroughly with distilled water before use.

SPECIAL PRECAUTIONS: Wear protective equipment (gloves, labcoats, and safety glasses) when working with HF. Do not use HF with glass labware. Perform all acid digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 170 to 800 L. Do not exceed 2 mg total dust loading on the filter.

SAMPLE PREPARATION:

3. Open the cassette and transfer the filter to the filtering apparatus on top of a 47-mm filter.
4. Add 3 mL deionized water to the sample filter, allow it to stand 3 min, apply vacuum to transfer the extract to the holding vessel and repeat with an additional 3 mL water.
5. Transfer the extracts to a 10-mL volumetric flask, add 1.0 mL 20% Na_2SO_4, dilute to volume, and analyze for soluble tungsten (step 19).
6. Digest the filters and residue in a covered PTFE beaker with 5.0 mL conc. HNO_3 and 5.0 mL conc. HF at 150 °C.
7. Remove the beaker cover and reduce the volume to 2 mL (150 °C).
8. Remove from heat, cool, add 10 mL 1% HCl, and agitate for 5 min.
9. Filter through an additional 47-mm filter (the filtrate may be analyzed for cobalt).
10. Digest the filter and residue in a PTFE beaker with 5.0 mL conc. HNO_3 and 5.0 mL conc. HF at 150 °C.
11. Remove the beaker cover and reduce the volume to 2 mL (150 °C). If filter residue is visible, add additional HNO_3 and HF (2 mL each).
12. Take to dryness at 100 °C.

13. Dissolve residue in beaker with 2.5 mL 0.5 M NaOH and 2.5 mL 20% Na_2SO_4 at 100 °C (15 min).
14. Transfer to a 25-mL volumetric flask and dilute to volume.

CALIBRATION AND QUALITY CONTROL:

15. Calibrate with at least five working standards over the range 0.03 to 12 mg W per sample.
    a. Add known amounts of calibration stock solution to 100-mL volumetric flasks containing 10 mL 0.5 M NaOH and 10 mL 20% Na_2SO_4; dilute to volume with distilled, deionized water.
    b. Analyze together with samples and blanks.
    c. Prepare calibration graph (absorbance vs. solution concentration, µg/mL).
16. Analyze three quality control blind spikes and three analyst spikes to ensure that the recovery and calibration graph are in control.

MEASUREMENT:

17. Set spectrophotometer to conditions on page 7074-1.
18. Aspirate standards and samples. Record absorbance readings.
19. If the absorbance values for the samples are outside of the range of the standards, dilute the solutions with 0.05 M NaOH/2% Na_2SO_4 solution, reanalyze and use the appropriate dilution factor in calculations.

CALCULATIONS:

20. Determine the solution concentrations of tungsten in the sample, C_s (µg/mL), and average media blank, C_b (µg/mL), from the calibration graph.
21. Using the solution volumes, mL, of the sample (V_s) and media blank (V_b), calculate the concentration of tungsten, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

This method is based on NIOSH P&CAM 271 [3,4] and was further evaluated and ruggedized under contract [2]. Lab testing with spiked samples over the ranges of 0.17 to 0.8 mg per sample (soluble) and 0.34 to 7.9 mg per sample (insoluble) gave precision (s_r) of 0.079 (soluble) and 0.076 (insoluble) [2]. Both soluble and insoluble tungsten species collected on filters were stable for two weeks [2].

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Tungsten and Cemented Tungsten Carbide, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-227 (1977).
[2] Carlin, L.M., G. Colovos, D. Garland, M. Jamin, M. Klenck, T. Long, and C. Nelson. Analytical Methods Evaluation and Validation: Arsenic, Nickel, Tungsten, Vanadium, Talc and Wood Dust, NIOSH Contract No. 210-79-0060 (1981), available as Order No. PB 83-155325 from NTIS, Springfield, VA 22161.
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 4, P&CAM 271, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[4] Hull, R.D. Analysis of Tungsten by Atomic Absorption Spectrophotometry: A Feasibility Study, NIOSH, DPSE, MRB, IMDS Technical Report (December, 1977).

METHOD WRITTEN BY: R. DeLon Hull, NIOSH/DPSE; additional data obtained under NIOSH Contract 210-79-0060.

FORMULA: ca. $C_{10}H_{16}$ (e.g., pinene, dipentene, and other terpenes)
M.W.: ca. 135

TURPENTINE

METHOD: 1551
ISSUED: 2/15/84

OSHA: 100 ppm
NIOSH: Group III Pesticide [1]
ACGIH: 100 ppm; STEL 150 ppm
(100 ppm = 560 mg/m³ @ NTP)

PROPERTIES: liquid; d 0.860 to 0.875 @ 15 °C;
BP 150 to 180 °C;
VP 0.67 kPa (5 mm Hg; 6580 ppm) @ 20 °C;
lower explosive limit 0.8% v/v in air

SYNONYMS: Gumspirits, wood turpentine; oil of turpentine; CAS #8006-64-2.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L @ 560 mg/m³
-MAX: 10 L

SHIPMENT: routine

SAMPLE STABILITY: at least 1 week @ 25 °C

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: required; 1 to 10 mL

ACCURACY

RANGE STUDIED: 264 to 1107 mg/m³ [2]

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.055 [2]

ANALYSIS

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: turpentine (all components)

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 225 °C
-DETECTOR: 250 °C
-COLUMN: 50 to 250 °C @ 8°/min

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: glass, 3 m x 6 mm, 10% SP-2100 on 80/100 mesh Supelcoport or 30 m x 0.32 mm ID fused silica capillary coated with DB-1

CALIBRATION: solutions of bulk turpentine in CS_2

RANGE: 0.5 to 20 mg per sample

ESTIMATED LOD: 0.1 mg per sample [4]

PRECISION (s_r): 0.013 [2]

APPLICABILITY: The working range is 50 to 2000 mg/m³ for a 10-L air sample. Turpentine is widely used as a solvent in paints, varnishes and lacquers.

INTERFERENCES: The chief constituents of turpentine are pinene isomers, diterpene and other $C_{10}H_{16}$ terpenes. Naphtha mixtures containing C_9-C_{11} alkanes or alkyl-substituted benzenes could cause interferences with the turpentine mixture. GC column and conditions should then be optimized for maximum resolution.

OTHER METHODS: This is Method S88 [3] in a revised format.

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REAGENTS:

1. Eluent: Carbon disulfide,* chromatographic quality, containing 0.8% v/v undecane, 0.1% v/v octane or other suitable internal standard.
2. Turpentine, bulk sample.
3. Nitrogen or helium, purified.
4. Hydrogen, prepurified.
5. Air, filtered.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1551-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Volumetric flasks, 10-mL.
7. Pipet, volumetric, 1.0-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 1 to 10 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
   NOTE: Retain the glass wool plug if an estimate of aerosol is needed.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.5 to 20 mg turpentine per sample.
   a. Add known amounts of the turpentine bulk sample to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of sum of peak areas of turpentine to peak area of internal standard).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.

b. Inject a known amount of aliquots of the turpentine bulk sample directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg turpentine recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1551-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.
    NOTE: Compare chromatograms of the air samples and the turpentine bulk sample for evidence of qualitative differences and possible interferences.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of turpentine found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of turpentine in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S88 [3] was issued on March 14, 1975, and validated over the range 264 to 1107 mg/m³ at 24 °C and 766 mm Hg using 10-L air samples [2]. Turpentine oil, double rectified (Fisher Scientific Co.; BP 150 to 170 °C; d 0.868 g/mL) in a calibrated syringe drive was used to generate turpentine atmospheres in dry air. Overall precision, s_r, was 0.055 with average recovery of 99%, representing a non-significant bias. Desorption efficiency was 0.95 in the range 2.8 to 11.3 mg per sample. The chromatographic column used was 6 ft x 1/8 in stainless steel packed with 1.5% OV-101 on 100/120 mesh Chromosorb W. Breakthrough (5% on back section) occurred at 126 min when sampling an atmosphere containing 1107 mg/m³ turpentine at 0.19 L/min at 0% RH.

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure During Manufacture and Formulation of Pesticides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-174 (1978).
[2] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 2., S88, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[4] User check, UBTL, NIOSH Sequence #4121-O,P (unpublished, December 2, 1983).

METHOD REVISED BY: Ardith A Grote, NIOSH/DPSE; S88 originally validated under NIOSH Contract CDC-99-74-45.

FORMULA: CH_2=CHBr; C_2H_3Br

M.W.: 106.96

VINYL BROMIDE

METHOD: 1009
ISSUED: 2/15/84

OSHA: 1 ppm; C 5 ppm
NIOSH: 1 ppm [1]
ACGIH: 5 ppm; suspect carcinogen [2]
(1 ppm = 4.37 mg/m³ @ NTP)

PROPERTIES [4]: d 1.493 g/mL @ 20 °C; BP 15.8 °C;
MP -137.8 °C;
VP 141 kPa (1054 mm Hg) @ 20 °C

SYNONYMS: bromoethene; bromoethylene; CAS #593-60-2.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal,
400 mg/200 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 2 L @ 4.4 mg/m³ (1 ppm)
-MAX: 10 L

SHIPMENT: no special precautions

SAMPLE STABILITY: at least 14 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1.32 to 56.5 mg/m³ [3]
(6-L samples)

BIAS: 0.021 [5]

OVERALL PRECISION (s_r): 0.090 (1.3 to 6.4 mg/m³) [3];
0.063 (6.4 to 56 mg/m³)

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: vinyl bromide

DESORPTION: 15 mL ethanol; 30 min ultrasonic agitation

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 140 °C
-DETECTOR: 240 °C
-PROGRAM: 3 min @ 50 °C, 40 °C/min to 225 °C, 5 min hold

CARRIER GAS: N_2 or He, 25 mL/min

COLUMN: nickel, 6 m x 2 mm ID, 10% FFAP on 80/100 mesh Chromosorb W AW DMCS

CALIBRATION: vinyl bromide in ethanol

RANGE: 8 to 335 µg per sample

ESTIMATED LOD: not determined

PRECISION (s_r): 0.040 [3]

APPLICABILITY: For 6-L samples, 0.3 ppm is lowest concentration providing analytical precision (s_r) < 0.1. For 10-L sample collected at high temperature and humidity, upper concentration limit is 30 ppm.

INTERFERENCES: Presence of other volatile compounds may interfere with collection of vinyl bromide or reduce capacity of sorbent tube. Under stated chromatographic conditions, ethylene, acetylene, and ethylene dibromide are separated from vinyl bromide; bromine is not separated.

OTHER METHODS: This is Method P&CAM 349 [3] in a revised format.

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REAGENTS:

1. Ethanol, absolute.*
2. Vinyl bromide (liquid), ≥ 98% purity.*
3. Calibration stock solution, ca. 30 µg/µL.
   a. Accurately weigh ca. 5 mL ethanol in a stoppered 10-mL volumetric flask.
   b. Chill (0 °C) the flask, vinyl bromide and a 1-mL gas-tight syringe.
   c. Transfer 0.2 mL vinyl bromide to the volumetric flask with the gas-tight syringe.
   d. Allow flask to return to room temperature. Reweigh and calculate solution concentration.

   NOTE: Prepare fresh daily, in duplicate. Solutions may be stable if refrigerated but stability data are not available.
4. Nitrogen, purified.
5. Hydrogen, prepurified.
6. Air, filtered.

*See Special Precautions.

EQUIPMENT:

1. Samplers: glass tube, 10 cm long, 8 mm OD, 6 mm ID, with flame-sealed ends containing glass wool plug; front, 400-mg section of 20/40 mesh activated (600 °C) coconut shell charcoal; urethane foam plug; rear, 200-mg section of charcoal; and rear urethane foam plug. Typical pressure drop 0.3 kPa at 0.2 L/min; must be < 3.4 kPa at sampling flow rate. Tubes are commercially available.
2. Personal sampling pumps, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Ultrasonic bath.
4. Gas chromatograph, FID, integrator and column (page 1009-1).
5. Vials, glass, 25-mL, crimp seals or caps with PTFE-lined silicone rubber septa.
6. Pipet, 15-mL, with pipet bulb.
7. Syringes, 10-µL, readable to 0.1 µL; 1-mL, gas-tight, with valve.
8. Balance, readable to 1 mg.
9. Flasks, volumetric, 2-, 5-, 10- and 25-mL.
10. File, triangular.
11. Ice.

SPECIAL PRECAUTIONS: Ethanol (flash point = 12 °C) is a fire hazard.

Vinyl bromide is suspect carcinogen [1,2]. Prepare samples and standards in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 2 to 10 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 15.0 mL ethanol to each vial. Attach crimp cap to each vial.
7. Place vials in an ultrasonic bath for 30 min.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 1 to 350 µg vinyl bromide per sample.
   a. Add known amounts of calibration stock solution to ethanol in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. µg vinyl bromide).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. µg vinyl bromide recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1009-1. Inject sample aliquot manually using solvent flush technique or with autosampler. Under these conditions, retention time is about 3.0 min.
    NOTE: If peak area is above the linear range of the working standards, dilute with ethanol, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE) of vinyl bromide found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of vinyl bromide in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Analytical precision was determined by analyzing spiked sampling media. Average desorption efficiency was 0.910. Breakthrough volume was 10 L for a concentration of 130 mg/m³ at 40 °C and >80% RH. Overall precision, bias, and storage stability were determined by sampling and analyzing generated atmospheres. Generated concentrations were independently verified. Reference [5] provides more specific information.

REFERENCES:

[1] Current Intelligence Bulletin: Vinyl Halides - Carcinogenicity, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-102 (1979).
[2] TLVs-Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment with Intended Changes for 1983-84, American Conference of Governmental Industrial Hygienists, Cincinnati, OH (1983).

[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 7, P&CAM 349, U.S. Department of Health and Human Services, Publ. (NIOSH) 82-100 (1982).
[4] Dreisbach, R. D. Physical Properties of Chemical Compounds, Advances in Chemistry Series, No. 29, American Chemical Society, Washington, DC, 278 (1961).
[5] Spafford, R. B. and H. K. Dillon. Analytical Methods Evaluation and Validation for Vinylidene Fluoride, Vinyl Bromide, Vinyl Fluoride, Benzenethiol, and n-Octanethiol: Research Report for Vinyl Bromide, NIOSH Contract No. 210-79-0100, Southern Research Institute, Birmingham, AL, available from NTIS, Springfield VA (1981).

METHOD REVISED BY: R. Alan Lunsford, Ph.D., NIOSH/DPSE; data obtained under NIOSH Contract 210-79-0100.

FORMULA: CH_2=CHCl; C_2H_3Cl

M.W.: 62.50

VINYL CHLORIDE

METHOD: 1007
ISSUED: 2/15/84

OSHA: 1 ppm; C 5 ppm
NIOSH: minimum measurable
ACGIH: 5 ppm (human carcinogen) [1]
(1 ppm = 2.56 mg/m³ @ NTP)

PROPERTIES: BP -14 °C; vapor density 2.2 (air = 1)

SYNONYMS: chloroethylene; chloroethene; CAS #75-01-4.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(2 tandem tubes, each with 150 mg activated coconut charcoal)

FLOW RATE: 0.05 L/min

VOL-MIN: 0.7 L
-MAX: 5 L

SHIPMENT: separate primary and backup tubes and cap each

SAMPLE STABILITY: 10 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1 to 64 mg/m³ [2]

BIAS: -6% of calculated concentration [2]

OVERALL PRECISION (s_r): 0.06 [2]

MEASUREMENT

!
!TECHNIQUE: GAS CHROMATOGRAPHY, FID
!
!ANALYTE: vinyl chloride
!
!DESORPTION: 1 mL carbon disulfide; 30 min
!
!INJECTION ALIQUOT: 5 µL
!
!COLUMN: stainless steel, 6.1 m x 3.2 mm, 10%
! SE-30 on 80/100 mesh Chromosorb W
! (AW-DMCS)
!
!CARRIER GAS: He, 40 mL/min
!
!TEMPERATURE-INJECTOR: 230 °C
! -DETECTOR: 230 °C
! -COLUMN: 60 °C
!
!CALIBRATION: solutions of vinyl chloride in CS_2
!
!RANGE: 0.002 to 0.2 mg per sample [2]
!
!ESTIMATED LOD: 0.00004 mg per sample [2]
!
!PRECISION (s_r): not determined
!

APPLICABILITY: The working range is 0.4 to 40 mg/m³ (0.16 to 16 ppm) for a 5-L air sample. The method is applicable to 15-min samples at concentrations of 1 ppm or higher.

INTERFERENCES: Other than the possibility of loss of sample upon storage of two weeks or more at room temperature, none have been noted.

OTHER METHODS: This is a revision of P&CAM 178 [3].

REAGENTS:

1. Carbon disulfide,* chromatographic quality.
2. Vinyl chloride,*, 99.9%, in lecture bottle fitted with valve and septum.
3. Calibration stock solution, 0.26 mg/mL.
   a. Insert the tip of a gas syringe containing 1 mL vinyl chloride gas under the surface of 5 mL CS_2 in a 10-mL volumetric flask.
   b. Open the valve of the syringe and withdraw the plunger to pull CS_2 into the barrel. (As vinyl chloride dissolves, a vacuum will be created, pulling CS_2 into the syringe.)
   c. Push the solution from the syringe into the flask. Rinse the syringe twice with 1-mL portions of CS_2 and add the washings to the flask.
   d. Dilute to the mark with CS_2.
4. Helium, purified.
5. Hydrogen, purified.
6. Air, filtered.

*See Special Precautions.

EQUIPMENT:

1. Sampler: two tandem glass tubes, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, each containing 150 mg of 20/40 mesh activated (600 °C) coconut shell charcoal. A silylated glass wool plug precedes the charcoal beds and a 3-mm urethane foam plug follows the charcoal beds. Plastic caps are included for sealing after use. Pressure drop across each tube at 1 L/min airflow must be less than 3.4 kPa.
   NOTE: A pair of two-section (100 mg/50 mg) tubes may be used.
2. Personal sampling pump, 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 1007-1).
4. File.
5. Bent wire for removing plugs from sampling tube.
6. Vials, 2-mL, glass with PTFE-lined septa and crimp-on seals.
7. Volumetric flasks, 10-mL, with polyethylene stoppers.
8. Pipettes, delivery, 1.0-mL, graduated in 0.1-mL increments, 2- and 5-mL, with pipet bulb.
9. Air sampling bags, Tedlar, 10-L.
10. Gas syringe, with gas-tight valve, 0.1- and 1-mL.
11. Syringe, 10-µL, with 0.1-µL graduations.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); work with it only in a hood.

Vinyl chloride is a human carcinogen [1].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the tubes immediately before sampling. Attach two tubes, with ends touching, with a short piece of tubing. Label one tube as the back tube and insert the back tube into the flexible tubing attached to the personal sampling pump.
3. Sample at 0.05 L/min for 15 to 100 min. Do not sample more than 5 L of air.
4. Separate the primary and backup tubes and cap each tube for shipment.

SAMPLE PREPARATION:

5. Add 1.0 mL CS_2 to an empty vial. Loosely cap the vial.
6. Score each sampler tube with a file in front of the glass wool plug. Break the tube at the score line.

7. Transfer the charcoal from the front and back tubes to separate vials. Discard the glass wool and foam plugs. Seal the vials with septum caps immediately.
8. Allow to stand for 30 min, with occasional agitation. Analyze the sample within the next 30-min period.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate with at least five working standards covering the range 0.0002 to 0.2 mg per sample.
   a. Add known amounts of calibration stock solution to CS_2 in 10-mL volumetric flasks and dilute to the marks, using serial dilution as appropriate.
      NOTE: Working standards can be stored at -20 °C for at least three days.
   b. Analyze together with samples and blanks (steps 12 and 13).
   c. Prepare calibration graphs of peak area vs. quantity (mg) of vinyl chloride per tube and peak area vs. quantity (ng) per injection.
10. Determine desorption efficiency (DE) at least once for each lot of charcoal used in the calibration range (step 9). Prepare three tubes at each of five levels plus three media blanks.
    a. Prepare three atmospheres of vinyl chloride in air by injecting 0.01, 0.08, and 0.2 mL vinyl chloride gas into 10 L air in Tedlar bags. The resulting concentrations are approximately 2.6, 21 and 52 mg/m^3.
    b. Following steps 1 through 4, sample these atmospheres according to the following scheme:

Concentration in Bag (mg/m^3)	Volume Sampled (L)	Quantity of Vinyl Chloride (mg)
2.6	0.8	0.002
	2.2	0.006
21	0.8	0.017
	2.2	0.046
52	2.5	0.13

    Obtain three samples at each level.
    c. Desorb (steps 6 through 8) and analyze together with working standards (steps 12 and 13). No vinyl chloride should be found on the back tubes.
    d. Analyze the atmospheres in the bags (steps 12 and 13) using 1-mL gas samples. Read from the calibration graph the quantity (ng) per injection, which for a 1-mL injection of gas is numerically equal to the concentration in mg/m^3.
    e. Calculate DE from the mass (mg) of vinyl chloride on the front tube (W_f), the average blank (B), the concentration of vinyl chloride in the synthetic atmospheres (C_s, mg/m^3), and the volume of air sampled (V, L):

$$DE = \frac{(W_f - B) \cdot 10^3}{(C_s)(V)}$$

    f. Prepare a graph of DE vs. mass found ($W_f - B$).
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

12. Set the gas chromatogrph according to manufacturer's instructions and to conditions given on page 1007-1. Inject sample aliquot manually using solvent flush technique or with autosampler. The retention time of vinyl chloride is about 1.7 min.
    NOTE: If peak area is above the linear range of the working standards, dilute with CS_2, reanalyze and apply the appropriate dilution factor in calculations.
13. Measure peak area.

CALCULATIONS:

14. Determine the mass, mg (corrected for DE) of vinyl chloride found in the sample front (W_f) and back (W_b) tubes, and in the average media blank (B).
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of vinyl chloride in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - 2B) \cdot 10^3}{V}, \ mg/m^3$$

EVALUATION OF METHOD:

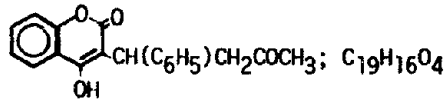
The method was evaluated using single 150-mg sampling tubes with 100-mg front beds and 50-mg back beds [2]. At four concentrations between 1 and 64 mg/m^3, the pooled relative standard deviation was 0.06 and the measurements averaged 94% of the concentrations calculated from the volumes of vinyl chloride and air used for the atmospheres sampled; samples at the 3-µg level showed no loss of vinyl chloride when stored for 12 days at room temperature or 19 days at -20 °C. There may be significant loss of vinyl chloride from samples stored for 14 days at room temperature [4]. The 1% breakthrough capacity for a 150-mg bed of coconut charcoal challenged at 100 mL/min with vinyl chloride in air at 16 mg/m^3 and a relative humidity of 70% was 4.6 L [5].

REFERENCES:

[1] TLVs - Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment with Intended Changes for 1983-84, ACGIH, Cincinnati, OH (1983).
[2] Hill, R. H., Jr., C. S. McCammon, A. T. Saalwaechter, A. W. Teass, and W. J. Woodfin. Anal. Chem., 48, 1395-1398 (1976).
[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 178, U.S. Department of Health and Human Services, Publ. (NIOSH) 77-157-A (1977).
[4] Cuddeback, J. E., W. R. Burg, and S. R. Birch, Environ. Sci. Technol., 9, 1168-1171 (1975).
[5] Matsumura, Y. Ind. Health, 18, 61-67 (1980).

METHOD REVISED BY: A. W. Teass, Ph.D., NIOSH/DPSE.

FORMULA:



M.W.: 308.32

WARFARIN

METHOD: 5002
ISSUED: 2/15/84

OSHA: 0.1 mg/m³
NIOSH: Group I Pesticide [1]
ACGIH: 0.1 mg/m³; STEL 0.3 mg/m³

PROPERTIES: solid, MP 161 °C;
VP not available

SYNONYMS: 3-(α-acetonylbenzyl)-4-hydroxycoumarin; CAS #81-81-2.

SAMPLING

SAMPLER: FILTER
(1-µm PTFE membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 250 L
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: 93% recovery after 7 days @ 25 °C [2]

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: desirable; 1 to 5 g

ACCURACY

RANGE STUDIED: 0.054 to 0.24 mg/m³ [2]
(408-L samples)

BIAS: none identified [2]

OVERALL PRECISION (s_r): 0.056 [2]

MEASUREMENT

!TECHNIQUE: HPLC, UV DETECTION
!
!ANALYTE: Warfarin
!
!EXTRACTION: 5 mL methanol; swirl
!
!INJECTION VOLUME: 20 µL
!
!COLUMN: C_{18} reverse phase, 10-µm packing,
! 25 to 30 cm
!
!MOBILE PHASE: 30% 0.0025 N phosphoric acid and
! 70% methanol, isocratic,
! 1.5mL/min, ambient temperature
!
!DETECTION: UV absorption @ 280 nm
!
!CALIBRATION: solutions of Warfarin in methanol
!
!RANGE: 20 to 200 µg per sample
!
!ESTIMATED LOD: 2.5 µg per sample
!
!PRECISION (s_r): 0.016 [2]
!
!
!

APPLICABILITY: The working range is 0.05 to 0.5 mg/m³ for a 400-L air sample.

INTERFERENCES: No interferences have been studied.

OTHER METHODS: This is P&CAM 313 [3] in a new format. Analytical methods for Warfarin in some rodenticides [4] and in drugs [5] are available; these are spectrophotometric methods for bulk materials.

REAGENTS:

1. Warfarin, 99%.*
2. Methanol, HPLC grade.*
3. Water, HPLC grade.
4. Phosphoric acid, 85%.*
5. Calibration stock solution, 2 mg/mL.* Dissolve 20.0 mg Warfarin in 10 mL methanol.
6. Mobile phase component, 0.0025 N phosphoric acid. Dissolve 0.06 mL 85% phosphoric acid in 1 L water.

*See Special Precautions.

EQUIPMENT:

1. Sampler: 37-mm diameter PTFE membrane filter, 1-µm pore size, and cellulose backup pad in two-piece filter holder held together with tape or shrinkable band.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. High pressure liquid chromatograph with 20 to 50-µL injection loop; 25 to 30 cm, 10-µm C_{18} column; UV absorption detector at 280 nm; and integrator.
4. Jars, squat form, 60-mL, ointment, with PTFE film gaskets and screw caps.
5. Tweezers.
6. Pipet, 5-mL, and pipet bulb.
7. Syringes, microliter.
8. Volumetric flasks, 10-mL and 1-L.

SPECIAL PRECAUTIONS: Methanol is flammable and toxic. Use in fume hood and away from ignition sources.

Warfarin is toxic and can be absorbed through the skin.

Phosphoric acid is corrosive. Use gloves, goggles and other appropriate equipment to prevent eye contact and repeated or prolonged skin contact. Wash skin with water and change clothes if contact occurs.

SAMPLING:

1. Calibrate each personal sampling pump with a representatave sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a sample size of 250 to 1000 L. Do not exceed a total loading of 2 mg on the filter.

SAMPLE PREPARATION:

3. Transfer filter with tweezers to jar.
4. Add 5.0 mL methanol. Cap the jar. Swirl to wet filter thoroughly.

CALIBRATION AND QUALITY CONTROL:

5. Calibrate daily with at least five working standards covering the range 4 to 120 µg Warfarin per sample.
   a. Add aliquots (2 to 60 µL) of calibration stock solution to 5 mL methanol in ointment jars.
   b. Analyze the working standards together with the samples and blanks (steps 7 and 8). NOTE: Duplicate injections should differ by no more than 3% in peak area.
   c. Prepare a calibration graph (peak area vs. µg Warfarin).
6. Determine recovery at least once in the calibration range (step 5). Prepare three filters at each of five levels plus three media blanks.
   a. Inject known volumes of calibration stock solution onto blank filters with a microliter syringe. Include media blanks.

b. Allow the filters to air dry overnight.
c. Analyze the filters (steps 3, 4, 7 and 8).
d. Prepare a graph of recovery vs. µg of Warfarin recovered.

MEASUREMENT:

7. Set liquid chromatograph to following conditions (typical; some variation possible):
   a. 1.5 mL/min flow mobile phase: 30% 0.0025 N phosphoric acid, 70% methanol, by volume.
   b. column: high resolution, analytical, octadecylsilyl reverse phase; 10-µm particle size; 25 to 30 cm; room temperature.
   c. injection: syringe or fixed volume loop, 20-µL.
   d. integrator: peak area, electronic or manual.
8. Make duplicate injections of each sample and working standard. Measure peak area.

CALCULATIONS:

9. Read the mass, µg (corrected for recovery) corresponding to the sample peak area on the sample (W) and average media blank (B) from the calibration graph.
10. Calculate the concentration, C (mg/m^3), of Warfarin in the volume of air sampled, V (L):

$$C = \frac{W - B}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method P&CAM 313 was issued on April 13, 1979 [3]. Lab testing was done with spiked samples and atmospheres dynamically generated by Wright dust feeder from commercial formulation; no adequate independent method was used for verification [2,6]. Storage stability was 93.5% for 60-µg samples stored seven days at ambient conditions. Collection efficiency = 100% for 408-L samples at 0.24 mg/m^3; no evidence of vapor in Tenax backup. Precision was as given on page 5002-1.

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure During the Manufacture and Formulation of Pesticides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-174 (1978).
[2] Backup Data Report, P&CAM 313, prepared under NIOSH Contract 210-76-0123 (unpublished, April, 1979).
[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 6, P&CAM 313, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).
[4] Horwitz, W., ed. Official Methods for Analysis of the AOAC, 13th ed., 85 (1980).
[5] Ibid, 628.
[6] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY: George M. Breuer, Ph.D., CIH, NIOSH/DPSE; P&CAM 313 developed under NIOSH Contract 210-76-0123.

FORMULA: Ag, Cd, Cr, Cu, Fe, Ni, Mn, Zn
(metals and oxides)

WELDING AND BRAZING FUME

METHOD: 7200
ISSUED: 2/15/84

OSHA: 5 mg/m³
NIOSH: no standard
ACGIH: 5 mg/m³ [1]

PROPERTIES: solid, stable, non-volatile particles; very small diameter

SYNONYMS: none.

SAMPLING

SAMPLER: FILTER
(0.8-µm cellulose ester membrane)

FLOW RATE: 1 L/min

VOL-MIN: 10 L
-MAX: 400 L

SHIPMENT: routine

SAMPLE STABILITY: stable at least 1 year @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD
BIAS: see EVALUATION OF METHOD
OVERALL PRECISION: see EVALUATION OF METHOD

MEASUREMENT

TECHNIQUE: X-RAY FLUORESCENCE

ANALYTE: Ag, Cd, Cr, Cu, Fe, Ni, Mn, Zn

INTENSITY RATIO: analyte to Co; or analyte to external standard containing analyte.

CALIBRATION: Cobalt-impregnated internal standard; laboratory-made fume standards, calibrated by atomic absorption spectrophotometry; optional external ratio standard

RANGE: 0.02 to 1 mg of each metal per sample [2,3]

ESTIMATED LOD: 2 µg of each metal per sample [2,3]

PRECISION (s_r): Table 1 [2,3].

APPLICABILITY: The working range is 0.2 to 10 mg/m³ for a 100-L air sample. The elemental composition of metal fumes from welding and brazing operations depends on the nature of the base metal, flux, and welding material used. Mild steel welding fume typically contains iron and manganese; stainless steel welding fumes may contain iron, nickel, chromium, and manganese; and brazing fumes usually contain cadmium, zinc, and copper [1,2].

INTERFERENCES: Interferences are easily controlled with wavelength-dispersive X-ray fluorescence, but are more severe with energy-dispersive systems. Also, the presence of cobalt in the fumes will require the use of a different ratio standard element.

OTHER METHODS: The method is based on P&CAM 345 [2,3]. Other methods applicable to welding fumes are 7300 (Elements), 70XX (atomic absorption), and 7600 (Chromium, hexavalent).

451 Preceding page blank

REAGENTS:

1. Elemental standards, powdered, containing only elements of interest (Spex Industries); or sample of welding fume.
2. Isopropanol.
3. Deionized water.
4. Internal ratio standard. Ion exchange filter paper (e.g., Gelman Acropor SA-6404), and cobalt standard solution (1000 µg/mL).
5. External ratio standard. Organometallic compounds for the various analyte elements, e.g., Cr 2,4-pentanedionate; Mn(II) cyclohexanebutyrate; Bis[dicarbonyl(MeCyclopentanedienyl)Iron]; Co(II)cyclohexanebutyrate; Bistriphenylphosphine $Ni(CO)_6$.
6. Polyester resin monomer, with hardener

EQUIPMENT:

1. Sampler: filter unit consisting of a 37-mm cellulose ester membrane filter, 0.8-µm pore size, in a three-piece cassette filter holder.
2. Personal sampling pump, 1 L/min, with flexible connecting tubing.
3. X-ray fluorescence spectrometer, energy- or wavelength-dispersive.
4. Buchner funnel, filtering apparatus with 0.45-µm cellulose ester membrane filter, and vacuum source.
5. Freezer mill.
6. Ultrasonic bath.
7. Glassware*: 1-L volumetric flask, 50-mL and 100-mL beakers, various pipets, 0.1- to 5-mL.
8. Atomic absorption spectrophotometer for initial calibration of standards, with deuterium background correction capability, and electrodeless discharge lamp or hollow cathode lamp for each element.

* Soak in 1 + 1 nitric acid and rinse thoroughly with deionized water before use

SPECIAL PRECAUTIONS: None.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Secure the end of a length of PVC tubing to the inside of the welder's helmet and attach the other end to the inlet of the sampler.
3. Sample at 1 L/min for a total sample size of 10 to 400 L. Visually inspect the samples and terminate sampling in time to avoid heavy deposition on the filter.
   NOTE: Heavy deposits (>2 mg) will not adhere to the filter and may be lost. In addition, heavy deposition may necessitate a non-linear calibration graph due to XRF shadowing.

SAMPLE PREPARATION:

4. Transfer the sample filters to XRF sample holders with tweezers, using care not to disturb the deposit.
   NOTE: Place the sample filter on top of a cobalt ratio standard filter (step B.a) if the internal ratio method is to be used.

CALIBRATION AND QUALITY CONTROL:

5. Obtain a qualitative scan of one of the filters to establish which elements are present in the samples. Set the XRF spectrometer parameters for the elements detected plus cobalt, according to the manufacturer's specifications.
6. Determine line overlap correction factors.
   Example: Cr Kβ emission interferes with the Mn Kα analyte line. From the spectrum of pure Cr, a factor, F, is found which relates the intensity of the Cr Kβ line (measured at the Mn Kα wavelength), to the intensity of the Cr Kα line:

$$F = \frac{\text{Cr K}\beta \text{ (at Mn K}\alpha \text{ wavelength)}}{\text{Cr K}\alpha \text{ (at Cr K}\alpha \text{ wavelength)}}$$

For the determination of the Mn Kα emission intensity, measure Cr at Cr Kα. Subtract the product of [Cr Kα emission] x F from the intensity measured at Mn Kα. The result is a measure of the Mn Kα intensity without the contribution from the line overlap interference of Cr.

7. Prepare a set of at least 5 standard filters, in quadruplicate, covering the range 0.02 to 1 mg per filter for the elements of interest.
   a. Add approximately 0.2 g powdered elemental standard to 1 L isopropanol. Mix ultrasonically for 30 min. Add a PTFE-coated stirring bar and stir continuously during use.
   b. Place a 0.45-µm cellulose ester membrane filter in the Buchner filtration apparatus. Add 50 mL isopropanol.
   c. Turn off the stirrer, shake the standard suspension vigorously three times and immediately withdraw an aliquot with a pipet (0.1 to 5 mL). Add the contents of the pipet to the isopropanol above the filter. Stir the liquid carefully with the pipet tip. Rinse the inside and outside of the pipet with a few mL isopropanol. Turn on the stirrer.
   d. Apply vacuum slowly to draw the suspension through the filter.
   e. Remove the filter. Let it air dry.
   f. Wet-ash two standard filters at each deposition level, including blank. Analyze the ashed filters (e.g., by atomic absorption spectrophotometry (AAS) or ICP AES - Method 7300). Retain the two remaining standard filters at each deposition level for analysis by XRF.
8. Prepare one of the following ratio stadnards:
   a. Internal ratio standard. Place the ion-exchange paper on the Buchner filtration assembly. Pour approximately 50 mL deionized water onto the filter, apply a slight vacuum, and collect the water in a second 100-mL beaker. Add 200 µL 1000 µg/mL cobalt standard solution to the collected water, pour into the Buchner filter device, and draw the liquid again through the filter with a slight vacuum. Collect the liquid with the first beaker and repeat, passing the liquid through the filter seven times. When completed, remove the filter to dry. Prepare identical cobalt-impregnated fiters for every position in the sample changer of the spectrometer.
      NOTE 1: Prior to use, analyze the cobalt-impregnated filters for cobalt by XRF to determine their similarity. They should give the same XRF analyte-line intensity for cobalt within normal statistical variation (i.e., the analyte-line intensity of any filter should differ from any other by an amount equal to the square root of the intensity in counts/sec).
      NOTE 2: Alternate method: Thoroughly mix about 0.2 g organocobalt compound, accurately weighed, with about 30 mL of polyester resin monomer. Mix in a few drops of hardener and pour equal amounts into clean 50-mL beakers. Prepare identical standards for each position in the XRF sample carrousel. When resin is competely hardened, break away glass. Mill the resin blocks to fit the XRF sampler holder and to present a flat surface to the X-rays.
   b. External ratio standard. Thoroughly mix about 0.2 g of organometallic compounds of interest into about 10 mL of polyester resin monomer. Mix in a few drops of hardener and allow to harden. Break away the glass. Mill to fit the XRF standard holder and to present a flat surface to the X-ray beam.

MEASUREMENT:

9. Load the sample, standard filters, and blank filters into the XRF instrument.
10. Obtain intensities of analyte elements and internal ratio standard or external ratio standard for each filter.

CALCULATIONS:

11. Divide analyte element line intensity on samples, standard filters, and blank filters by the internal ratio standard intensity of Co or by the external ratio standard intensity of the analyte element to calculate intensity ratio, R.
12. Prepare a calibration graph (mass of element, µg, on the standard filters vs. R (corrected for blank)).
13. Calculate the concentration, C (mg/m^3), of analyte element in the air volume sampled, V (L):

$$C = \frac{K(I - B - X)}{V}$$

where: K = slope in µg/(ratio intensity) of the standard calibration graph
I = XRF ratio intensity of the analyte line
B = corrections for XRF analyte-line background intensity and line overlap, if needed (ratio intensity)
X = XRF ratio intensity of the filter blank.

EVALUATION OF METHOD:

The method was developed using welding (shielded metal arc welding on stainless and mild steels) and brazing (StaFlo-45 brazing wire on copper) fume samples having loadings of 30-280 µg filter (as oxides). The method was validated for iron, nickel, chromium, and manganese [2,3,4], using the internal standard method. Copper, zinc, and cadmium were also evaluated but not validated. A 120-L sample will provide sufficient deposition to detect the above-mentioned elements at air concentrations of one-half the current TLV for the compounds.

Element	Range[1] (mg/m^3)	Detection Limit[2] (µg)	s_r (%)	Mean Bias[3] (%)	TLV [4] (mg/m^3)	Sensitivity[4] (relative intensity/µg)
Iron	0.05-0.50	1.5	0.07	5.9	5	178.1
Manganese	0.04-0.29	2.7	0.067	4.6	1	168.1
Chromium	0.04-0.42	1.8	0.068	12.3	0.5[5]	21.1
Nickel	0.02-0.14	1.5	0.071	6.8	1	47.2
Copper[6]	0.01-0.03	-	0.12	-	0.2	-
Zinc	0.05-0.06	-	0.043	-	5	-
Cadmium	0.3-5.0	-	0.063	-	C 0.05	-

[1]Based on a 120-L sample. Upper limit defined by highest validation sample; may be extended to approximately 2 mg/m^3 without a non-linear calibration curve.
[2]DL = $3A(I^{1/2})/120$ L where I is the filter blank intensity, and A is the slope of the calibration graph [(AI) = concentration in µg], as defined in [5].
[3]Mean of (100 x [AAS - XFR]/AAS), where AAS is the amount of metal determined by atomic absorption spectroscopy, from the four deposition levels.
[4]Defined as [analyte line intensity/cobalt line intensity]/[AAS result, µg/filter].
[5]Chromium (VI) compounds have a TLV of 0.05 mg/m^3 [4].
[6]PTFE filter holder required.

REFERENCES:
[1] TLVs - Threshold Limit Values for Chemical Substances and Physical Agents in the Workplace Environment with Intended Changes for 1983-84, Appendix B2, ACGIH, Cincinnati, OH (1983).
[2] Carsey, T. Feasibility Study of X-ray Fluorescence for Analysis of Welding and Brazing Fumes, available through NTIS (in press).
[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 7, U. S. Dept. of Health and Human Services Publ. (NIOSH) 82-100 (1982).
[4] Carsey, T. Standardization Techniques in X-ray Fluorescence, U.S. Department of Health and Human Services, (NIOSH) Internal Report (1981).
[5] Bertin, E. P. Principles and Practice of X-ray Spectrometric Analysis, 2nd ed., Plenum, NY (1975).

METHOD REVISED BY: Thomas P. Carsey, Ph.D., NIOSH/DPSE.

FORMULA: Zn

M.W.: 65.37 (Zn); 83.17 (ZnO)

ZINC and compounds, as Zn

METHOD: 7030
ISSUED: 2/15/84

OSHA: not established
NIOSH: 5 mg/m³ (ZnO); 15 mg/m³/15 min (ZnO)
ACGIH: 5 mg/m³, STEL 10 mg/m³ (ZnO fume)
10 mg/m³ (ZnO dust)

PROPERTIES: metal; valence 2; MP 419 °C (Zn); VP not significant

SYNONYMS: vary depending upon the compound; CAS #1314-13-2 (ZnO); CAS #7440-66-6 (Zn).

SAMPLING

SAMPLER: FILTER
(0.8-µm cellulose ester membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 2 L @ 5 mg/m³
-MAX: 400 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: not measured

OVERALL PRECISION (s_r): not measured

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, FLAME

ANALYTE: zinc

ASHING: conc. HNO_3, 6 mL; 140 °C

FINAL SOLUTION: 1% HNO_3, 100 mL

FLAME: air-acetylene, oxidizing

WAVELENGTH: 213.9 nm

BACKGROUND CORRECTION: D_2 or H_2 lamp, if needed

CALIBRATION: Zn^{++} in 10% HNO_3

RANGE: 10 to 100 µg per sample [1]

ESTIMATED LOD: 3 µg per sample [5]

PRECISION (s_r): 0.03 [1]

APPLICABILITY: The working range is 1 to 10 mg/m³ for a 10-L sample. This is an elemental analysis, not compound specific. Aliquots of the samples can be analyzed separately for many additional metals.

INTERFERENCES: None known.

OTHER METHODS: This method is a revision and replacement of P&CAM 173 for Zinc [1,4]. Method 7300 (plasma emission) is an alternate analytical method. Method 7502 (X-ray diffraction) is specific for ZnO.

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REAGENTS:

1. Nitric acid, conc.
2. Nitric acid, 1% (v/v). Add 10 mL conc. HNO_3 to 500 mL water; dilute to 1 L.
3. Calibration stock solution, 1000 µg Zn/mL. Commercial standard or dissolve 1.00 g Zn metal in minimum volume of (1+1) HCl; dilute to 1 L with 1% (v/v) HNO_3.
4. Air, filtered.
5. Acetylene.
6. Distilled or deionized water.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-µm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with air-acetylene burner head and zinc hollow cathode lamp or electrodeless discharge lamp.
4. Regulators, 2-stage, for air and acetylene.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.*
6. Volumetric flasks, 100-mL.*
7. Micropipets, 1 to 100 µL.*
8. Hotplate, surface temperature 140 °C.

*Clean with conc. HNO_3 and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Perform all acid digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a sample size of 2 to 400 L. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

NOTE: The following sample preparation gave quantitative recovery (see EVALUATION OF METHOD). Steps 4 through 9 of Method 7300 or other quantitative ashing techniques may be substituted, especially if several metals are to be determined on a single filter.

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
4. Add 6 mL conc. HNO_3 and cover with a watchglass. Start reagent blanks at this point.
5. Heat on hotplate (140 °C) until sample dissolves and a slightly yellow solution is produced. Add additional acid as needed to completely destroy organic material.
6. When the sample solution is clear, remove watchglass and rinse into the beaker with 1% HNO_3.
7. Place the beakers on the hotplate and allow to go to dryness.
8. When sample is dry, rinse walls of beaker with 10 mL 10% HNO_3. Reheat 5 min to dissolve the residue, then allow to air cool.
9. Transfer the solution quantitatively to a 100-mL volumetric flask and dilute to volume with distilled or deionized water.
   NOTE: Dilute to a smaller volume, e.g., 10 mL, if required for sensitivity of analysis for other metals in the sample.

CALIBRATION AND QUALITY CONTROL:

10. Add known amounts, covering the range 0 to 100 µg Zn per sample, of calibration stock solution to 100-mL volumetric flasks and dilute to volume with 1% HNO_3.
11. Analyze the working standards together with the samples and blanks (steps 16 and 17).
12. Prepare a calibration graph of absorbance vs. solution concentration (µg/mL).

13. Aspirate a standard for every 10 samples to check instrument drift.
14. Check recoveries with at least one spiked media blank per 10 samples.
15. Use method of additions occasionally to check for interferences.

MEASUREMENT:

16. Set spectrophotometer according to manufacturer's recommendations and to conditions on page 7030-1.
    NOTE: Non-atomic absorption may require the use of D_2 or H_2 continuum background correction in some samples.
17. Aspirate standards and samples. Record absorbance readings.
    NOTE: If the absorbance values for the samples are outside of the range of the standards, dilute the solutions with 1% HNO_3, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

18. Using the measured absorbances, calculate the corresponding concentrations (µg/mL) of zinc in the sample, C_s, and average media blank, C_b, from the calibration graph.
19. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration, C (mg/m^3), of zinc in the volume of air sampled, V (L):

$$C = \frac{(C_s V_s - C_b V_b)}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Estimated LOD was 3 µg Zn per sample [5].

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd ed., V. 5, P&CAM 173, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[2] Winefordner, J. D., Ed., Spectrochemical Methods of Analysis, John Wiley & Sons (1971).
[3] Analytical Methods for Atomic Absorption Spectrophotometry, Perkin-Elmer (1976).
[4] Criteria for a Recommended Standard...Occupational Exposure to Zinc Oxide, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-104 (1976).
[5] User check, UBTL, NIOSH Seq.# 3990-P (unpublished, November 29, 1983).

METHOD WRITTEN BY: Mark Millson and R. DeLon Hull, NIOSH/DPSE.

FORMULA: ZnO

M.W.: 81.38

ZINC OXIDE

METHOD: 7502
ISSUED: 2/15/84

OSHA: 5 mg/m³ (fume)
NIOSH: 5 mg/m³; 15 mg/m³/15 min [1] (fume)
ACGIH: 5 mg/m³; STEL 10 mg/m³ (fume)

PROPERTIES: solid; d 5.61 g/cm³ @ 25°C; MP 1975 °C

SYNONYMS: China white; zinc white; zincite; CAS #1314-13-2.

SAMPLING

SAMPLER: FILTER
(0.8-µm PVC membrane, 25-mm diameter, in open-face cassette)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 10 L
-MAX: 400 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: high-volume air sample required

ACCURACY

RANGE STUDIED: 0.1 to 11 mg/m³ [2,4]
(180-L samples)

BIAS: not significant [4,8,9]

OVERALL PRECISION (s_r): 0.088 [4]

MEASUREMENT

TECHNIQUE: X-RAY POWDER DIFFRACTION

ANALYTE: crystalline zinc oxide; direct analysis on filter

XRD: Cu target X-ray tube
Optimize for intensity; 1° slit
Graphite monochromator; scintillation detector
Slow step scan, 0.02°/10 sec
Integrated intensity with background subtraction

CALIBRATION: suspensions of ZnO in 2-propanol

RANGE: 50 to 2000 µg per sample

ESTIMATED LOD: 5 µg per sample

PRECISION (s_r): 0.15 @ 1 mg/m³ ;
0.05 for greater than 2 mg/m³

APPLICABILITY: The working range is 0.25 to 10 mg/m³ for a 200-L air sample. The method does not distinguish zinc oxide fume from zinc oxide dust. The fume sample is assumed to be of small particle size and no cyclone is used.

INTERFERENCES: Major interferences include Fe_2O_3, Zn, $Zn(NH_3)_2Cl_2$, $(NH_4)_3ZnCl_5$, $(NH_4)_2ZnCl_4$ and $(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$; these are resolved by using alternate analyte peaks. Particle size affects intensity measurements.

OTHER METHODS: This method combines and replaces Methods P&CAM 222 [2] and S316 [3]. The criteria document contains an elemental analysis for zinc [1].

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REAGENTS:

1. Zinc oxide, ACS reagent grade. Average particle size between 0.5 µm and 10 µm.
2. 2-Propanol.
3. Desiccant.
4. Glue or tape for securing filters to XRD holders.

EQUIPMENT:

1. Sampler: polyvinyl chloride (PVC) or PVC-acrylonitrile membrane filters, 25-mm diameter, 0.8-µm pore size; three-piece filter cassette.
   NOTE: An extension cowl on the filter cassette is desirable to produce a more uniform deposit and to prevent contamination of the open-face filter during sampling.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. High-volume sampling pump, 10 L/min.
4. X-ray powder diffractometer equipped with copper target X-ray tube and scintillation detector.
5. Reference specimen (mica, Arkansas stone or other stable standard) for data normalization.
6. Filtration apparatus and side arm vacuum flask with 25-mm filter holder.
7. Analytical balance (0.01 mg); magnetic stirrer; ultrasonic bath or probe; volumetric pipettes and flasks; desiccator; reagent bottles with ground glass stoppers; drying oven; polyethylene wash bottle.

SPECIAL PRECAUTIONS: none

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample open-face at 1 to 3 L/min for a total sample size of 10 to 400 L. Do not exceed 2 mg total dust loading on the filter.
3. Take a high-volume (4000-L) air sample using a clean sampler and high-volume sampling pump in the same area as the personal sample(s) for qualitative identification.

SAMPLE PREPARATION:

4. Mount field samples and blanks on XRD sample holders using appropriate methods for securing the sample to the XRD holder.

CALIBRATION AND QUALITY CONTROL:

5. Prepare two suspensions of ZnO in 2-propanol by weighing 10 mg and 50 mg of the dry powder to the nearest 0.01 mg. Quantitatively transfer to a 1-L glass-stoppered bottle using 1 L 2-propanol.
6. Suspend the powder in 2-propanol by using an ultrasonic probe or bath for 20 min. Immediately move the flask to a magnetic stirrer with thermally-insulated top and add a stirring bar to the suspension. Cool the solution to room temperature before withdrawing aliquots.
7. Prepare a series of standard filters using the 10 and 50 mg/L suspensions. Using appropriate pipets, prepare a sufficient number of standards in triplicate to cover the analytical range (or sample range if known). Standards at 20, 30, 50 100, 200 and 500 µg are usually sufficient.

8. Mount a filter on the filtration apparatus. Place several mL 2-propanol on the filter surface. Turn off the stirrer and shake vigorously by hand. Within a few seconds of setting the bottle down, remove the lid and withdraw an aliquot from the center of the suspension. Do not adjust the volume in the pipet by expelling part of the suspension. If more than the desired aliquot is withdrawn, return all of the suspension to the bottle, rinse and dry the pipet. Transfer the aliquot from the pipet to the filter funnel, keeping the tip of the pipet near the surface of the liquid but not submerged.
9. Rinse the pipet with several mL of 2-propanol, draining the rinse into the funnel. Repeat the rinse several more times.
10. Apply vacuum and rapidly filter the suspension. Leave vacuum on until filter is dry. Do not wash down the sides of the funnel after the deposit is in place to avoid disturbing it. Transfer the filter to the XRD sample mount.
11. Perform step scans on the standards using the same diffraction peaks and instrumental conditions as for samples (step 16). The resulting intensities for standards, I_x^o, are normalized in the following procedure.
12. Determine the net count, I_r, of the reference specimen before or after each unknown, standard or blank is scanned. Use a diffraction peak of high intensity that can be measured rapidly but reproducibly (less than 1% s_r). Select a convenient normalization scale factor, N, which is approximately equivalent to the net count for the reference specimen peak. This factor never changes and should be used for all measurements made on a particular diffractometer. Calculate and record the normalized intensity, $\hat{I}_x^o$, for the analyte or silver peaks on each sample, field blank, media blank and standard:

$$\hat{I}_x^o = \frac{I_x^o}{I_r} \cdot N.$$

NOTE: Normalizing to the reference specimen intensity compensates for long-term drift in X-ray tube intensity. If intensity measurements are stable, the reference specimen may be run less frequently. In this case, the net intensities of the analyte, I_x, should be normalized to the most recently measured reference intensity.

13. Prepare a calibration graph ($\hat{I}_x^o$ vs. µg analyte).
NOTE: Poor reproducibility at any given level indicates problems in the sample preparation technique and new standards should be made. The data should lie along a straight line. A weighted least squares ($1/\sigma^2$ weighting) is preferable. Curvature can be eliminated with absorption corrections based on the mass absorption coefficient of the analyte [5,6,7].
14. Determine the initial slope, m, of the linear portion of the calibration graph in counts/µg. The intercept, b, of the line with the $\hat{I}_x^o$ axis should be approximately zero.
NOTE: A large negative intercept indicates an error in determining the background. This may arise from incorrectly measuring the baseline or from interference by another phase at the angle of background measurement. A large positive intercept indicates an error in determining the baseline or that an impurity is included in the measured peak.

MEASUREMENT:

15. Obtain a qualitative X-ray diffraction scan (broad 2-theta range) of the high-volume respirable sample to determine the presence of ZnO and any matrix interference. The expected diffraction peaks are as follows:

ZnO Peak (2-Theta Degrees)		
Primary	Secondary	Tertiary
36.26	31.75	34.44

16. Analyze the sample filters by step-scanning the most intense interference-free diffraction peak of zinc oxide and determine the integrated intensity. Measure the background on each side of the peak for one half the time used for peak scanning and add the counts from each side for a total (average) background. Determine the 2-theta position of the background for each sample. The net count or intensity, I_x, is the difference between the peak integrated count and the total background count. The net intensity is normalized as in step 12 to obtain $\hat{I}_x$.
17. Scan each field blank over the same 2-theta range used for the analyte. These analyses serve only to verify that contamination of the filters has not occurred. The analyte peak should be absent.

CALCULATIONS:

18. The concentration of ZnO in the air sample is:

$$C = \frac{(\hat{I}_x - b)}{m \cdot V} \text{ , mg/m}^3$$

where: $\hat{I}_x$ = normalized intensity for sample peak
b = intercept of calibration graph ($\hat{I}_x^0$ vs. W)
m = slope of calibration graph (counts/µg)
V = air volume sampled (L).

In heavily-loaded samples, particularly those rich in heavy elements, X-ray absorption may cause reduced intensities and underestimation of ZnO. If this is suspected, an absorption correction can be made [6]. The collection filters and blanks are mounted on a smooth metal plate (substrate) for XRD quantitation. The substrate should have a non-interfering diffraction peak which is measured at the same time as the ZnO peak. By measuring the substrate peak on both samples and blanks, an absorption correction like that in the silica method (Method 7500) can be made. The absorption correction factor must be calculated for each sample from the formula in Method 7500 which takes into account the diffraction angles for the particular substrate chosen. Altree-Williams used a silver filter under the collection filter.

EVALUATION OF METHOD: In a comparison of this method with atomic absorption spetrophotometry [8,9], zinc was determined on 15 Gelman DM-800 filters containing added zinc oxide in the range 250 to 1000 µg. The average percent difference for the 15 pairs was 2.7%. Method S316 was validated with generated samples in the range of 2.4 to 9.9 mg/m³ [3,4,10]. A pooled s_r of 0.09 was found for 18 samples of 180 L collected from the aerosol.

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Zinc Oxide, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-104 (1975).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 222, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[3] Ibid, V. 4, S316, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1979).

[4] Zinc Oxide Fume, S316, Backup Data Report, NIOSH Contract No. 210-76-0123, available as "Ten NIOSH Analytical Methods, Set 3," Order No. PB 275-834 from National Technical Information Service, Springfield, VA 22161.

[5] Altree-Williams, S., J. Lee and N. V. Mezin. Quantitative X-ray Diffraction on Respirable Dust Collected on Nuclepore Filters, Annals of Occup. Hyg., 20, 109 (1977).

[6] Leroux, J. and C. Powers. Direct X-Ray Diffraction Quantitative Analysis of Quartz in Industrial Dust Films Deposited on Silver Membrane Filters, Occup. Health Rev., 21, 26 (1970).

[7] Williams, D. D. Direct Quantitative Diffractometric Analysis, Anal. Chem., 31, 1841 (1959).

[8] Haartz, J. C., M. L. Bolyard and M. T. Abell. Quantitation of Zinc Chloride and Zinc Oxide in Airborne Samples, paper presented at the American Industrial Hygiene Conference, Minneapolis, MN (June, 1975).

[9] Dollberg, D. D., M. T. Abell and B. A. Lange. Occupational Health Analytical Chemistry: Quantitation Using X-Ray Powder Diffraction, ACS Symposium Series, 120, 43 (1980).

[10] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY: D. D. Dollberg, Ph.D, and M. T. Abell, NIOSH/DPSE.

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delta–AMINOLEVULINIC ACID DEHYDRATASE in blood

FORMULA: none

METHOD: 8000

M.W.: none

ISSUED: 2/15/84

BIOLOGICAL INDICATOR OF: exposure to lead (Pb).

SYNONYMS: ALAD.

BIOLOGICAL SAMPLING	MEASUREMENT
SPECIMEN: venous whole blood	TECHNIQUE: ENZYMATIC, SPECTROPHOTOMETRIC
CONTAINER: heparinized vacuum tubes	ANALYTE: porphobilinogen (PBG)
VOLUME: 5-mL	INCUBATE: 0.2 mL whole blood hemolysate + ALA → PBG
SHIPMENT: in polyfoam packers with bagged ice or refrigerant	TERMINATE REACTION: with trichloroacetic acid
STABILITY: maintain samples @ 4 °C until analysis; analyze within 48 hrs of collection CAUTION: DO NOT FREEZE	COLOR FORMATION: with Ehrlich's reagent
	WAVELENGTH: 555 nm
CONTROLS: collect blood from non-exposed workers	CALIBRATION: calibrate spectrophotometer for photometric accuracy
	QUALITY CONTROL: compare with controls
	RANGE: 10 to 60 units/mL packed red blood cells
	PRECISION (s_r): 0.05

APPLICABILITY: Lead in small quantities is known to inhibit the enzyme δ-aminolevulinic acid dehydratase (ALAD) which converts δ-aminolevulinic acid (ALA) to porphobilinogen (PBG). This method is very sensitive to low level lead exposures making it useful as a biological monitor at low exposure levels. Chronic exposures are not distinguishable from acute exposures by this method.

INTERFERENCES: Some heavy metals like zinc, tin, mercury, cadmium, and silver and some organics like EDTA or succinylacetone, can inhibit ALAD in vitro but under circumstances which are unlikely to occur in the workplace. False positives may occur if samples are not analyzed within 48 hrs of collection.

OTHER METHODS: This is Method P&CAM 328 [5] in a revised format. Most literature methods follow this procedure using either of 2 different Ehrlich reagents [1,2,3,4].

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REAGENTS:

1. Phosphate-citrate buffer, 0.01 M:
   A. Dissolve 6.703 g $Na_2HPO_4 \cdot 7H_2O$ in distilled H_2O; dilute to 100 mL.
   B. Dissolve 5.25 g citric acid in distilled H_2O; dilute to 100 mL.
   C. Adjust the pH of solution A to 6.65 by adding solution B. Store at 4 °C (stable for 1 month).
2. δ-Aminolevulinic acid (ALA) solution, 0.01 M. Dissolve 16.8 mg δ-ALA-HCl in 10 mL of solution C above. Prepare fresh solution daily.
3. Ehrlich's reagent*. Dissolve 1.0 g p-dimethylaminobenzaldehyde in 30 mL glacial acid. Add 8 mL 70% perchloric acid; dilute to 50 mL with glacial acetic acid. This solution is stable for 6 hrs.
4. Trichloroacetic acid, 10%. Dissolve 10 g TCA in 50 mL distilled H_2O. Add 2.7 g mercuric chloride ($HgCl_2$) and dilute to 100 mL with distilled water. Stable at room temperature.

*See Special Precautions.

EQUIPMENT:

1. Spectrophotometer, with 1-cm light path capable of reading 2 mL sample at 555 nm.
2. Microhematocrit tubes, reader and centrifuge.
3. Centrifuge, table top clinical, and 15-mL conical tubes.
4. Waterbath, 37° ± 1 °C.
5. Mixer, vortex.
6. Pipets, serological, 1- and 2-mL, with pipet bulb.
7. Pipets, TC, 200-µL.
8. Balance, analytical.
9. pH meter.
10. Test tubes, disposable, 5-mL.

SPECIAL PRECAUTIONS: Prepare and store Ehrlich's reagent in fume hood.

SAMPLING:

1. Collect 5 mL venous whole blood in vacuum tubes containing heparin. Avoid hemolysis.
2. Ship samples in polyfoam packs containing bagged ice or refrigerant and store samples at 4 °C for no longer than 48 hrs before analysis.
   NOTE: Samples must not be frozen nor kept warmer than 20 °C.

CALIBRATION AND QUALITY CONTROL:

3. Calibrate the spectrophotometer for both wavelength and photometric accuracy according to manufacturer's instructions.
   NOTE: This assay does not make use of chemical standards. The extinction coefficient of the product of the reaction (PBG) is known; therefore, it is possible to calculate the concentration from the absorbance.

MEASUREMENT:

NOTE: Protect the sample from direct sunlight from this point on.

4. Mix 1.3 mL distilled water and 200 µL of sample in a small centrifuge tube.
5. Add 1.0 mL of ALA solution and mix.

6. Prepare a blank for each batch of samples by mixing 1.3 mL distilled water, 0.2 mL sample, 1.0 mL ALA solution, and 1.0 mL of TCA in a small centrifuge tube.
7. Incubate all tubes in a 37 °C waterbath for 60 min.
8. Remove from waterbath and terminate the reaction by adding 1.0 mL of TCA to all tubes except blank; mix on the vortex mixer.
9. Centrifuge at 1500 to 2000 rpm for 10 min.
10. Transfer 1.0 mL of clear supernatant, without disturbing the precipitate, to a clean test tube.
11. Add 1.0 mL of fresh Ehrlich's reagent. Mix and let stand 10 min.
12. Read absorbance at 555 nm using blank to set zero. Complete all readings within 15 min.
13. Fill microhematocrit tube with well-mixed whole blood samples and spin for 5 min. Read hematocrit using a hematocrit reader.

CALCULATIONS:

14. Express the ALAD concentration, C, in units ALAD (amount of enzyme activity required to produce 1 micromole PBG/min at 37 °C)/mL packed red blood cells (RBC), using the absorbance of the sample, A, and the hematocrit, H:

$$C = \frac{A \times 100 \times 18.82}{H}$$

NOTE: The factor 18.82 includes the extinction coefficient and dilution factors.

GUIDES TO INTERPRETATION:

The expected blood lead/ALAD relationship is [1]:

Blood Lead, µg/100 mL	ALAD ± s_r
30	32.3 ± 11.1
30–44	25.8 ± 9.1
45–59	18.0 ± 5.5
60	12.3 ± 3.5

EVALUATION OF METHOD:

The reproducibility of the method was found to average 5% over the above range. Weissberg, et al. [1] have a good discussion on the validity of the method for monitoring low lead exposure.

REFERENCES:

[1] Weissberg, J. B., Lipshuz, F. and Oski, F. A. δ-Aminolevulinic Acid Dehydratase Activity in Circulating Blood Cells, New Eng. J. Med., 284, 565-569 (1971).
[2] Bonsignore, D., Calissano, P. and Cartesegna, C. Un semplice metodo per la determinazione della δ-aminolevulinico-deidrasi mel sangue. Comportamento cel "enzima nell" intassicazione saturina, Med. Lavoro, 56, 199-205 (1965).
[3] Burch, H. B., and Siegel, A. L. Improved method for measurement of δ-aminolevulinic acid dehydratase in activity in human erythrocytes, Clin. Chem., 17, 1039-1041 (1971).
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[5] NIOSH Manual of Analytical Methods, 2nd ed., V. 6, P&CAM 328, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).

METHOD WRITTEN BY: Frederick C. Phipps and Larry K. Lowry, NIOSH/DBBS.

FORMULA:

$C_{12}H_{12}N_2$

M.W.: 184.24

BENZIDINE in urine (SCREENING TEST)

METHOD: 8304
ISSUED: 2/15/84

BIOLOGICAL INDICATOR OF: exposure to benzidine-based azo dyes.

SYNONYMS: [1,1'-biphenyl]-4,4'-diamine; CAS #92-87-5.

BIOLOGICAL SAMPLING	MEASUREMENT
SPECIMEN: 2 urine samples, 150 mL each, before and after 6 hrs of exposure	TECHNIQUE: VISIBLE ABSORPTION/THIN LAYER CHROMATOGRAPHY (TLC)
PRESERVATIVE: none	ANALYTE: 2,4,5-trinitrobenzene sulfonic acid derivative of benzidine
SHIPMENT: with dry ice in insulated container	WAVELENGTH: 400 nm
STABILITY: stable for 2 months @ -20 °C	TLC IDENTIFICATION: UV and visible, R_f = 0.41
CONTROLS: collect urine from non-exposed workers	ESTIMATED LOD: 0.1 µg/100 mL urine (visible absorption); 0.3 µg/100 mL urine (TLC)
	CALIBRATION: aqueous solutions of benzidine
	QUALITY CONTROL: frozen pooled urine
	RANGE: 0.1 to 20 µg/100 mL urine
	RECOVERY: 70% @ 0.5 µg/100 mL urine
	PRECISION (s_r): 0.12 @ 0.5 µg/100 mL urine

APPLICABILITY: This method is specific for aromatic amines and can be used to screen workers exposed to benzidine or benzidine-based azo dyes.

INTERFERENCES: In addition to false positives from other free aromatic amines, some drugs (e.g., antihistamines) contain free aromatic amines; however, these compounds do not produce R_f values corresponding to benzidine by TLC.

OTHER METHODS: This method replaces P&CAM 315 [1] with minor revisions. Method 8306 is a specific method for benzidine in urine by electron capture gas chromatography.

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REAGENTS:

1. Methyl alcohol.
2. Benzidine, 99% (CAUTION: CARCINOGEN).*
3. Benzidine stock solution, 500 µg/mL. Weigh 50 mg benzidine. Dissolve in methyl alcohol to make 100 mL solution. Stable one month at -8 °C.
4. Calibration stock solution, 10 µg/mL.* Dilute 1.00 mL benzidine stock solution to 50 mL with methyl alcohol. Prepare fresh daily.
5. Chloroform.
6. Hydrochloric acid.
   a. 1.0 N. Dilute 83 mL conc. HCl to 100 mL with distilled water.
   b. 0.1 N. Dilute 10 mL 1 N HCl to 100 mL with distilled water.
7. Sodium hydroxide, 1 N. Dissolve 40 g NaOH in water to make 1 L solution.
8. Sodium chloride, crystals.
9. Sodium acetate buffer, 2 M, pH 5.5. Titrate 2 M sodium acetate with 6 N HCl. Refrigerate.
10. 2,4,6-Trinitrobenzene sulfonic acid (TNBS), 0.1 g/mL. Dissolve 2.5 g TNBS in 25 mL distilled water. Stable seven days when stored in the dark.
11. Acetone.
12. Formic acid.
13. Nitrogen, compressed.
14. Chloroform:formic acid, 90:10 (v/v). Prepare fresh daily.

*See Special Precautions.

EQUIPMENT:

1. Polyethylene bottles, 250-mL.
2. Spectrophotometer for measuring absorbance at 400 nm and 1-mL semi-microcuvettes.
3. Centrifuge, 4000 rpm.
4. Rotator for mixing 25 x 200 mm test tubes.
5. pH meter.
6. TLC plates precoated with silica gel activated at 110 °C for 30 min, without fluorescence indicator (0.5 mm thickness).
7. Chromatographic TLC tank.
8. UV source for reading TLC plates.
9. Glass bottles, 180-mL, with PTFE-lined caps.
10. Pipettes, glass, 2-, 5- and 100-mL, with pipet bulb.
11. Separatory funnels, 125-mL.
12. Volumetric flasks, 25- and 100-mL (also 10-mL amber).
13. Culture tubes, glass with PTFE-lined caps (16 x 125 mm and 25 x 200 mm).
14. Micropipettes, 0.01-, 0.1- and 0.7-mL.
15. Pasteur pipettes.
16. Plastic gloves.
17. Dessicator.
18. pH paper (pH 2).

SPECIAL PRECAUTIONS: Benzidine is a known human carcinogen and appropriate precautions should be utilized to minimize exposure.

All wastes, including acetone rinses of dirty glassware should be collected and disposed of by approved methods.

SAMPLING:

1. Take pre- and post-shift spot urine samples (ca. 150 mL) in 250-mL polyethylene bottles.
2. Ship the samples with dry ice in an insulated container.

SAMPLE PREPARATION:

3. Defrost sample if frozen. Adjust the urine pH to between 5 and 6 with 1 N HCl or 1 N NaOH.
4. Pipet 100 mL urine into a 180-mL glass bottle. Start a blank control urine sample (100 mL) and two control urine samples (100 mL) spiked with benzidine (0.3 to 1.0 µg) at this point.
5. Add 0.2 g NaCl to the pH-adjusted urine.
6. Extract the urine with 10 mL chloroform for 2 min. If an emulsion forms centrifuge to separate the two phases. Collect and save the chloroform fraction.
7. Extract the urine twice more with 10-mL portions of chloroform. Combine the three chloroform fractions.
8. Reextract the combined chloroform mixture with 2 mL 0.1 N HCl for 30 min on a rotator.
9. Transfer the aqueous phase (≃ 2 mL) into a culture tube (16 x 125 mm) using a Pasteur pipet.
10. Add 2 mL pH 5.5 sodium acetate buffer and 0.7 mL of TNBS reagent, mix well, and let stand for 15 min at room temperature. Start reagent blank (2 mL 0.1 N HCl, 2 mL pH 5.5 sodium acetate buffer, and 0.7 mL TNBS reagent).

CALIBRATION AND QUALITY CONTROL:

11. Prepare a series of working standards in the range 0 to 20 µg benzidine/100 mL urine by adding aliquots of calibration stock solution to 100-mL portions of control urine (urine pool previously shown to have <0.1 µg benzidine/100 mL urine).
12. Prepare and analyze the working standards (steps 3 through 10 and 14 through 16).
13. Prepare a calibration graph, plotting benzidine concentration (µg/100 mL urine) vs. absorbance at 400 nm.

MEASUREMENT:

14. Add 2 mL $CHCl_3$ to the extract in step 10 and shake for 1 min.
15. Measure the absorbance vs. the reagent blank of the organic phase at 400 nm. Retain the organic phase for the benzidine-TLC confirmation (steps 16 through 19) if the sample contains more than 0.3 µg/100 mL.
16. Concentrate the organic phase containing the TNBS-amine derivative by evaporating with nitrogen to ca. 0.2 mL.
17. Spot 10 µL of the concentrated organic phase on an activated silica gel TLC plate.
18. Develop the plate in 90:10 chloroform:formic acid.
19. Compare the R_f of the unknown amine derivative with that of a benzidine-spiked derivative. Benzidine produces a spot with R_f = 0.41 which is yellow in visible light and dark under UV (254 nm) light.

CALCULATIONS:

20. Obtain the concentration of the analyte in the urine sample by comparing its absorbance with the calibration graph.

    NOTE: Corrections for extraction efficiency are not needed since standards are prepared in urine and both standards and samples are treated the same way.

GUIDES TO INTERPRETATION:

In this laboratory, normal ranges of urine specimens from NIOSH employees not exposed to benzidine or aromatic amines were:

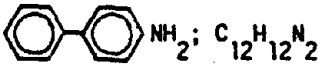
Number of Urine Specimens	Aromatic Amine Conc. (µg/100 mL)
10	<0.1
2	0.1 to 0.2
1	0.2
1	0.3

Benzidine was not detected by TLC in any of the 14 urine specimens (LOD = 0.3 µg/100 mL).

EVALUATION OF METHOD:
Ten spiked urine specimens containing 0.5 µg benzidine/100 mL urine each were analyzed. Precision, s_r, for the 10 specimens was 0.12.

REFERENCES:
[1] NIOSH Manual of Analytical Methods, 2nd. ed., V. 5, P&CAM 315, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).

METHOD WRITTEN BY: William P. Tolos, NIOSH/DBBS.

FORMULA:  $C_{12}H_{12}N_2$

M.W.: 184.24

BENZIDINE IN URINE

METHOD: 8306
ISSUED: 2/15/84

BIOLOGICAL INDICATOR OF: exposures to benzidine and benzidine-based azo dyes.

SYNONYMS: [1,1'-biphenyl]-4,4'-diamine; CAS #92-87-5.

BIOLOGICAL SAMPLING	MEASUREMENT
SPECIMEN: urine, 2 to 3 hrs after exposure	TECHNIQUE: GAS CHROMATOGRAPHY, ECD
VOLUME: 100 mL in polyethylene bottle	ANALYTE: N,N'-diheptafluorobutyryl benzidine
PRESERVATIVE: 2 drops 12 N HCl after collection	INJECTION: Grob type-splitless
	VOLUME: 3 µL
SHIPMENT: frozen and shipped in dry ice	
	COLUMN: 15 m x 0.25 mm I.D. capillary; WCOT-SE-54
STABILITY: unknown	
	CARRIER GAS: 5% methane in argon, 1 mL/min
CONTROLS: at least 3 urine specimens from non-exposed individuals per study; 1 per 10 samples	TEMPERATURE-INJECTOR: 260 °C -DETECTOR: 350 °C -COLUMN: 120 °C for 2 min; 40°/min to 280°; hold 6 min
	CALIBRATION: solutions of benzidine in benzene with internal standard
	QUALITY CONTROL: spiked urine corrected for creatinine content
	RANGE: 10 to 1000 µg/L
	RECOVERY: 92%
	ESTIMATED LOD: 5 µg/L
	PRECISION (s_r): 0.11

APPLICABILITY: This procedure is useful for monitoring exposures to benzidine or benzidine-based azo dyes which are absorbed via the skin, lung, or gastrointestinal tract, and whose metabolites are benzidine or acetylbenzidine. This procedure quantitates benzidine, N-acetylbenzidine, N,N'-diacetylbenzidine, as conjugates of benzidine. Maximum urinary levels occur 2 to 3 hrs after exposure [1].

INTERFERENCES: None known.

OTHER METHODS: This method is based on references [2] and [3]. Method 8304 is a less specific, screening method [4].

REAGENTS:

1. Hydrochloric acid, conc. (sp. gr. 1.18).
2. Sodium hydroxide, 10 N. Dissolve 400 g NaOH in 1:1 methanol:water (v/v) to make 1 L solution. CAUTION: EXOTHERMIC REACTION.
3. Sodium hydroxide, 5 N. Dilute 10 N with 1:1 methanol:water.
4. Acetone, hexane, methanol, and benzene*, pesticide grade.
5. Hexane:benzene, 3:2 (v/v).
6. Sodium sulfate (anhydrous) extracted in Soxhlet extractor for 24 hrs with benzene.
7. Trimethylamine stock solution.
   a. Dissolve 2 g $(CH_3)_3NHCl$ in 5 mL 5 N NaOH. CAUTION: EXOTHERMIC REACTION.
   b. Extract four times with 5-mL portions of benzene.
   c. Percolate each 5 mL extract through a 2-cm anhydrous sodium sulfate column (keep in the dark and refrigerated when not in use). Reagent stability unknown.
8. Trimethylamine working solution. Dilute trimethylamine stock solution 1:20 with benzene. Reagent stability unknown.
9. Benzidine stock solution, 100 µg/mL.* Dissolve 10 mg benzidine, accurately weighed, in benzene to make 100 mL solution. Refrigerate. Discard if a color develops.
10. Methylene dianiline stock solution, 100 µg/mL. Dissolve 10 mg methylenedianiline, accurately weighed, in benzene to make 100 mL solution. Refrigerate. Discard if color develops.
11. Derivatized methylenedianiline stock solution, 1 µg/mL.
    a. Add 0.1 mL methylenedianiline stock solution to 1.5 mL benzene and 0.5 mL trimethylamine working solution.
    b. Derivatize and wash (steps 12 and 13).

EQUIPMENT:

1. Bottles, polyethylene, 125-mL.
2. Gas chromatograph with $_{28}Ni^{63}$ electron capture detector, temperature programming, capillary column option, Grob-type injection system, and electronic integrator.
3. Shaker and rotator.
4. Evaporator and vortex mixer.
5. Centrifuge (refrigerated optional).
6. Waterbath with a temperature range 30 to 100 °C.
7. Soxhlet extractor.
8. Culture tubes, 25 x 200 mm, 20 x 125 mm, and 16 x 150 mm, with PTFE-lined screw caps.*
9. Pipettes, 1-, 5- and 10-mL and Pasteur (disposable).*
10. Graduated centrifuge tubes, 15-mL, glass-stoppered.*
11. Volumetric flasks.*

*Wash with detergent, clean with chromic acid, rinse with distilled water, acetone, and benzene.

REAGENTS:

c. Percolate the solution through 2 cm anhydrous sodium sulfate.
d. Dilute to 10.0 mL with benzene. Stable at least one month.

12. Florisil, PR grade, 60/100 mesh; activated at 650 °C.
    a. Extract 24 hrs in a Soxhlet extractor with benzene.
    b. Heat to 130 °C for 24 hrs.
    c. Cool and add 10 g distilled water/100 g Florisil. Shake overnight.
13. Buffer. Dissolve 136 g KH_2PO_4 in 900 mL H_2O. Adjust to pH 6 with 10 N NaOH. Dilute to 1 L with H_2O and extract once with 100 mL benzene.
14. Paraffin oil.
15. Heptafluorobutyric anhydride.
16. Nitrogen gas, compressed.

*See Special Precautions.

SPECIAL PRECAUTIONS: Benzidine and benzene are documented human carcinogens and must be handled in compliance with 29 CFR 1910.1005 and 1910.1028).

SAMPLING:

1. Collect a spot urine sample in a polyethylene bottle. Add 2 drops 12 N HCl as a preservative.
2. Freeze the samples and ship in an insulated container with dry ice.
3. Keep the samples frozen until analysis.

SAMPLE PREPARATION:

4. Perform a creatinine determination on an aliquot of the sample (e.g., [4]).
5. Pipet 10 mL of the urine specimen into a 50-mL culture tube containing 10 mL 10 N NaOH.
6. Seal the tube and incubate 2 hrs at 80 °C.
7. Cool to room temperature, add 20 mL benzene, seal, and shake 1 hr.
8. Remove the benzene layer and percolate it through a 2-cm column of anhydrous sodium sulfate. Collect the eluate in a 25 x 200 mm culture tube.
9. Repeat step 8 twice. Combine the extracts.
10. Add three or four drops of paraffin oil to the extracts and concentrate the extracts to near dryness under a gentle stream of nitrogen.
11. Add 1.5 mL benzene and 0.5 mL trimethylamine working solution.
12. Add 50 µL heptafluorobutyric anhydride. Seal and place in a 50 °C waterbath for 20 min. Cool to room temperature.
13. Wash the derivatized extract.
    a. Add 2 mL pH 6 buffer solution. Seal and shake 2 min.
    b. Centrifuge 2 min. Discard the bottom (aqueous) layer.
    c. Repeat the washing with two additional 2-mL portions of pH 6 buffer.
14. Place a small glass wool plug in a chromatographic column and add 1.6 g Florisil. Top with 2 cm anhydrous sodium sulfate. Wash the column with 50 mL hexane.
15. Add the buffer-washed, derivatized extract to the Florisil column. Rinse the culture tube twice with ca. 2 mL benzene and add the rinsings to the Florisil column.
16. When the top of the extract is in the sodium sulfate layer, add 10 mL 3:2 (v/v) hexane:benzene. Discard the eluate.
17. Elute the N,N'-diheptafluorobutyryl benzidine with 15 mL benzene.
18. Add 0.5 mL derivatized methylenedianiline stock solution to the eluate. Concentrate to 10 mL under a gentle stream of nitrogen.

CALIBRATION AND QUALITY CONTROL:

19. Prepare six working standards containing between 0 and 10 µg benzidine.
    a. Add aliquots of benzidine stock solution to 1.5 mL benzene and 0.5 mL trimethylamine working solution.
    b. Perform steps 12 and 13.
    c. Percolate the benzene layer through 2 cm anhydrous sodium sulfate.
    d. Add 0.5 mL derivatized methylenedianiline stock solution.
    e. Dilute to 10.0 mL with benzene.
    f. Analyze the working standards together with samples and blanks (steps 21 and 22).
    g. Prepare calibration graph (concentration of standards vs. ratio of peak areas due to benzidine and methylenedianiline).
20. Analyze a spiked urine for every 10 samples (minimum three per study).

MEASUREMENT:

21. Set up the chromatograph according to manufacturer's recommendations and conditions given on page 8306-1.
22. Inject 3 µL derivatized sample extract (step 18). Measure peak areas due to both methylenedianiline and benzidine. Calculate the ratio of peak areas (benzidine to methylenedianiline). The t_r of methylenedianiline is 7.6 min while the t_r of benzidine is 8.0 min under these conditions.

CALCULATIONS:

23. Determine benzidine urine concentrations (µg/mL) by comparing the ratio of benzidine methylenedianiline peak areas for the samples to those obtained for standards on the calibration graph. Report the results as µg benzidine/g creatinine.

GUIDES FOR INTERPRETATION:

Benzidine is an OSHA-regulated human carcinogen. Although no specific standard has been set, the fact that benzidine is a human carcinogen means it or its metabolites should not be detected in urine or any other physiological fluid. However, a level of 0.010 µg/mL has been suggested as an indicator of excessive exposure [1].

REFERENCES:

[1] Baselt, R. C. Biological Monitoring Methods for Industrial Chemicals, 43, Biomedical Publications, Davis, CA (1980).

[2] Nony, C. R., and M. C. Bowman. Trace Analysis of Potentially Carcinogenic Metabolites of an Azo Dye and Pigment in Hamster and Human Urine as Determined by Two Chromatographic Procedures, J. Chromatographic Sci., 18, 64 (February, 1980).

[3] Benzidine-Based Dyes, 46, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-109 (1980).

[4] Tietz, N. W. Fundamentals of Clinical Chemistry, 2nd ed., 994-997, W. B. Saunders Co., Philadelphia, PA (1976).

METHOD WRITTEN BY: Anthony W. Smallwood, Karl E. DeBord, and Larry K. Lowry, Ph.D., NIOSH/DBBS.

(1) 2-BUTANONE, (2) ETHANOL and (3) TOLUENE IN BLOOD

METHOD: 8002
ISSUED: 2/15/84

FORMULA: (1) $CH_3CH_2COCH_3$; C_4H_8O; 72.12
and (2) CH_3CH_2OH; $C_2H_6O_2$; 46.07
M.W.:

(3) CH_3; C_7H_8; 92.15

BIOLOGICAL INDICATOR OF: exposure to 2-butanone, ethanol, and toluene.

SYNONYMS: (1) MEK, methyl ethyl ketone; CAS# 78-93-3.
(2) ethyl alcohol; CAS# 64-17-5.
(3) methyl benzene; CAS# 108-88-3.

BIOLOGICAL SAMPLING	MEASUREMENT
SPECIMEN: venous blood, after 2 or more hrs of exposure	!TECHNIQUE: GAS CHROMATOGRAPHY, FID
CONTAINER: 5-mL heparin-coated vacuum tube	!ANALYTE: MEK, ethanol, toluene (simultaneous)
SHIPMENT: air express @ 4 °C	!TEMPERATURE-INJECTION: 150 °C !-DETECTOR: 200 °C !-COLUMN: 85 °C (4 min), 85 to 220 °C @ 16 °C/min, 220 °C(4 min)
STABILITY: stable @ 4 °C for 3 weeks	
CONTROLS: pre-shift whole blood samples as well as whole blood samples from non-exposed controls	!CARRIER GAS: helium, 25 mL/min !COLUMN: glass, 3 m x 2 mm ID, 5% Carbowax 20 M on 100/120 mesh Chromosorb WHP !CALIBRATION: blood standards containing analytes !RANGE: (1) 0.1 to 8 µg/mL; ! (2) 0.01 to 0.6 mg/mL; ! (3) 1 to 600 µg/mL !RECOVERIES: (1) 0.90 @ 2 µg/mL blood; ! (2) 0.98 @ 0.05 mg/mL blood; ! (3) 0.93 @ 2 µg/mL blood !PRECISION (s_r): (1) 0.095 (1 µg/mL blood); ! (2) 0.056 (0.1 mg/mL blood); ! (3) 0.098 (1 µg/mL blood)

APPLICABILITY: MEK and toluene are commonly found in trace amounts in humans working in the paint spray industry. Occasionally, traces of ethanol are also present. This method can be used in screening workers exposed to these central nervous system depressants.

INTERFERENCES: Ethanol concentrations in excess of the stated range may interfere with the MEK peaks at low concentration (< 0.2 µg MEK/mL blood). Ethanol in excess of the stated range also increases blood toluene concentration [1]. When substances other than the analytes are suspected to be present in the blood, record their identities to determine possible interferences [2].

OTHER METHODS: None are known that can determine these constituents simultaneously. Other methods require extraction or distillation for concentration of trace amounts of these chemicals in blood.

REAGENTS:

1. 2-Butanone, calibration stock solution (3.864 mg/mL). Dilute 1.2 mL 2-butanone to 250 mL with distilled water. Stable several months at 4 °C.
2. Toluene, calibration stock solution (3.81 mg/mL). Dilute 1.1 mL toluene to 250 mL with acetone. Stable several months.
3. Ethanol, calibration stock solution (157.8 mg/mL). Dilute 10 mL absolute ethanol to 50 mL with distilled water. Stable several months at 4 °C.
4. Citric acid.
5. Sodium citrate.
6. Dextrose.
7. Acetone.
8. Isobutanol, 8 µg/mL (aqueous), internal standard.
9. Acidum citricum dextrose solution (ACD). Accurately weigh 4.8 g citric acid, 13.2 g sodium citrate, and 14.7 g dextrose. Dissolve and dilute to 1 L with distilled water.
10. Blood (human), from blood centers or from individuals not exposed to the analytes.* Can be stored at 4 °C for three weeks.

*See Special Precautions.

EQUIPMENT:

1. Tubes, heparin-coated, vacuum, 5-mL.
2. Gas chromatograph with flame-ionization detector, electronic integrator, and column (page 8002-1).
3. Rotator for mixing blood specimens.
4. Vials, screw-cap septum with caps, 7-mL.
5. Septum discs, PTFE-lined.
6. Heater, Dri-block with temperature control (30 to 100 °C) to accommodate the 7-mL size vials.
7. Micropipettes, 100- to 1000-µL.
8. Syringes, gas-tight, 1-mL, with valve.
9. Syringes, tuberculin, disposable, 1-mL, with 21-gauge needle.
10. Volumetric flasks, 50- and 250-mL.

SPECIAL PRECAUTIONS: All human blood products should be considered potentially hazardous and be handled as an infectious agent. The risk is to hepatitis.

SAMPLING:

1. Collect 5 mL venous whole blood in a vacuum tube containing heparin. Invert the tube gently several times to mix.
2. Ship samples in polyfoam packs containing bagged ice or refrigerant.

SAMPLE PREPARATION:

3. Pipet 0.5 mL ACD solution and 0.25 mL isobutanol solution into a 7-mL glass screw-cap vial and mix.
4. Using a tuberculin syringe with a 21-gauge needle, draw 0.25 mL of blood from the vacuum tube and add to the vial.

5. Secure the PTFE-lined septum disc and cap tightly to the vial.
6. Mix the solution very slowly on a rotator for 5 min.

CALIBRATION AND QUALITY CONTROL:

7. Prepare working standard solutions. Pipet 2 mL from each of the calibration stock solutions into separate 200-mL volumetric flasks. Dilute to the mark with deionized water. The resultant concentrations are 38.1 and 38.6 µg/mL for toluene and MEK, respectively; and 1.58 mg/mL for ethanol. Prepare fresh standards every 92 hrs.
8. Make blood standards at 5 different concentrations ranging from 0 to 8 µg MEK and toluene/mL blood and from 0 to 500 µg ethanol/mL blood. Add aliquots of the working standards to 2 mL blood with a microliter syringe. Prepare fresh blood standards every 92 hrs and store at 4 °C.
9. Analyze the blood standards (steps 3 through 6 and 12 through 14).
10. Plot the concentrations (µg/mL) vs. the ratio of the peak areas of each analyte to the peak areas of the internal standard (isobutanol) on the same chromatogram to establish the calibration graph.
11. Include a blood control with each run.

MEASUREMENT:

12. Heat the sealed vial in a block heater at 60 °C for 15 min.
13. Remove a 1-mL aliquot of the head space vapor inside the sealed vial with a heated 60 °C gas-tight syringe and inject into the gas chromatograph.
    NOTE: Temperature control of blood and syringe is very important for accurate results. Heat the gas-tight syringe to 60 °C in an oven.
14. Measure the peak areas. Divide the peak area for each analyte by the peak area for the internal standard on the same chromatogram.

CALCULATIONS:

15. Determine the concentrations of 2-butanone, toluene and ethanol in blood from the calibration graph.

GUIDES TO INTERPRETATION:

1. Blood-alcohol analyses are usually reported in mg/dL or % w/v blood alcohol concentration (BAC). Thus, a BAC may be reported as 300 µg/mL or 30 mg/dL, or 0.03 g/dL, or 0.03% w/v. Legal blood alcohol concentrations are reported in reference [3].
2. Single toluene inhalation exposures of 50 and 100 ppm in air for 3 hrs produced average blood (human) toluene concentration of 1.6 and 3.9 ppm, respectively [4]. Another study reported blood toluene levels ranging from 4.1 to 7.3 ppm for exposure to 200 ppm toluene in air [5].

EVALUATION OF METHOD:

1. Ten spiked replicate blood samples at the blood level of 1 µg/mL for 2-butanone and toluene and 10 µg/mL for ethanol were analyzed. The precision data obtained for each analyte were 9.5, 9.8, and 5.6%, respectively.
2. Average recoveries of 10 replicate blood samples for 2-butanone, toluene and ethanol were 90, 93 and 98%, at the level of 2 µg/mL of 2-butanone, 2 µg/mL toluene, respectively, and 0.05 mg/mL of ethanol, respectively, in pooled blood.

REFERENCES:
[1] Waldron, H. A., N. Cherry, and J. D. Johnson. The Effects of Ethanol on Blood Toluene Concentrations, Int. Arch. Occup. Environ. Health, 51, 365-369 (1983).
[2] Hachenberg, H. and A. P. Schmidt. Gas Chromatographic Headspace Analysis, 2nd ed., Heyden and Son Ltd., Philadelphia, PA (1979).
[3] Dubowski, K. M. Alcohol Analysis: Clinical Laboratory Aspects, Part II, Laboratory Management, 27-36 (April, 1982).
[4] Stewart, R. D., C. L. Hake, H. V. Forster, A. J. Lebrun, J. E. Peterson, and A. Wu. Toluene: Development of a Biologic Standard for Industrial Worker by Breath Analysis, NIOSH Contract Report No. 99-72-84 (1975).
[5] Lauwerys, R. R. Industrial Chemical Exposure: Guidelines for Biological Monitoring, Biomedical Publications, Davis, CA (1983).

METHOD WRITTEN BY: William P. Tolos, NIOSH/DBBS.

FORMULA: F

M.W.: 19.00

FLUORIDE IN URINE

METHOD: 8308
ISSUED: 2/15/84

BIOLOGICAL INDICATOR OF: exposure to inorganic fluorides [1,2].

SYNONYMS: none.

BIOLOGICAL SAMPLING	MEASUREMENT
SPECIMEN: urine, pre- and post-shift	TECHNIQUE: ION SELECTIVE ELECTRODE (ISE)
VOLUME: 50 mL in chemically clean polyethylene bottles	ANALYTE: fluoride ion (F^-)
	DILUTION: mix equal volumes of urine with TISAB
PRESERVATIVE: 0.2 g EDTA added to bottles before collection	CALIBRATION: solutions of sodium fluoride in water
SHIPMENT: in insulated containers using bagged refrigerant	QUALITY CONTROL: spiked urine pools; correct for creatinine content
STABILITY: 2 weeks @ 4 °C, longer if frozen	RANGE: 1 to 100 mg/L urine
CONTROLS: collect 3 sets of specimens from unexposed workers (pre- and post-shift)	ESTIMATED LOD: 0.1 mg/L urine
	RECOVERY: 0.95 [3]
	PRECISION (s_r): 0.04

APPLICABILITY: Any fluorine-containing substances that can be metabolized to fluoride (F^-) can be monitored using this procedure. Inorganic compounds of fluoride can be absorbed by the body resulting in the excretion of fluoride ions as sodium fluoride. Dietary and domestic water sources of fluoride must be considered, as well as dental treatments.

INTERFERENCES: Hydroxide, the only positive interference, is eliminated by use of the buffer. Negative interferences from complexation of fluoride by cations, such as calcium, are minimized by EDTA preservative and the high ionic strength buffer.

OTHER METHODS: This method is P&CAM 114 [4] in a revised format. Other methods that have been used are those described in the NIOSH criteria documents on inorganic fluorides [1] and hydrogen fluoride [2].

REAGENTS:

1. Distilled or deionized water.
2. Sodium citrate ($Na_3C_6H_3O_7 \cdot 2H_2O$).
3. Ethylene dinitrilotetracetic acid (EDTA), disodium salt.
4. Acetic acid, glacial.
5. Sodium chloride.
6. Sodium hydroxide, 5 M. Dissolve 20 g NaOH in distilled water; dilute to 100 mL.
7. Sodium fluoride.
8. Calibration stock solution, 100 µg F^-/mL. Dissolve 0.2211 g dry sodium fluoride in distilled water. Make 1000 mL solution.
9. Total ionic strength activity buffer (TISAB), pH 5. Add 57 mL glacial acetic acid, 58 g sodium chloride, and 0.30 g sodium citrate to a 1-L beaker containing 500 mL distilled water. Stir to dissolve. Place beaker in waterbath for cooling. Slowly add 5 M sodium hydroxide until the pH is between 5.0 and 5.5. Cool to room temperature; dilute to 1 L with distilled water.

EQUIPMENT:

1. Polyethylene bottles, 125-mL, wide-mouth.
2. Fluoride ion specific electrode (ISE), with reference electrode.
3. pH/millivolt meter, reading to ± 0.5 mv.
4. Stirrer, magnetic.
5. Stirring bars, PTFE-coated.
6. Beakers, plastic, 50-mL.
7. pH electrode.
8. Pipets, appropriate sizes for standards.
9. Volumetric flasks for standards.
10. Waterbath.

SPECIAL PRECAUTIONS: None.

SAMPLING:

1. Collect pre- and post-shift spot urine samples in polyethylene bottles containing 0.2 g EDTA.
2. Ship samples in insulated container at about 4 °C using bagged refrigerant.

SAMPLE PREPARATION:

3. Perform a creatinine determination on an aliquot of the urine (e.g., [5]).

CALIBRATION AND QUALITY CONTROL:

4. Prepare at least five working standards in the range 0.1 to 100 µg F^-/mL by appropriate dilutions of the calibration stock solution with distilled water.
5. Analyze a set of working standards together with the samples and blanks (steps 9 through 12) starting with the lowest concentration.
   NOTE: Working standards, samples, and blanks must be analyzed under the same conditions, including temperature, for accurate results.
6. Prepare a calibration graph on three-cycle semi-log paper plotting millivolts on the linear scale and fluoride concentration, µg/mL, on the log scale.
7. Maintain standardization by running a standard with every 10 specimens.
8. Run a spiked urine control specimen with every 10 specimens to maintain quality assurance.
   NOTE: Urine used for spiked controls must be analyzed before use to determine background fluoride concentration.

MEASUREMENT:

9. Add 10 mL well-mixed urine and 10 mL TISAB to a 50-mL plastic beaker.
10. Place a small stirring bar into beaker and mix continuously on a magnetic stirrer at room temperature.
11. Immerse electrodes. Allow sample to mix for 2 to 3 min and then record millivolt reading.
12. Rinse electrodes and stirring bar thoroughly with distilled water and wipe dry with tissue before next sample analysis.

CALCULATIONS:

13. Convert the millivolt readings to fluoride concentration using the calibration graph.
14. Express fluoride concentration as mg F^-/g urinary creatinine.

GUIDES TO INTERPRETATION:

Urine concentrations of fluorides in normal non-occupationally exposed workers have been reported to range from 0.2 to 3.2 mg/L depending on dietary intake [6]. Preshift levels of less than 4 mg/g creatinine and post-shift levels of less than 7 mg/g creatinine appears to protect workers against bony fluorosis [7]. NIOSH has recommended that post-shift urine specimens should not exceed 7 mg/L (corrected to a specific gravity of 1.024) and pre-shift specimens should not exceed 4 mg/L (1.024) [1,2].

EVALUATION OF METHOD:

No formal method evaluation has been reported; however, Tusl [3] reported recoveries of added fluoride from 94 to 100%. Precision based on analysis of 25 specimens in triplicate is estimated to be better than $s_r = 0.04$.

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Inorganic Fluorides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-103 (1976).
[2] Criteria for a Recommended Standard...Occupational Exposure to Hydrogen Fluoride, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-143 (1976).
[3] Tusl, J. Direct determination of fluoride in human urine using fluoride electrode, Clin. Chim. Acta, 27, 216-218 (1970).
[4] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 114, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[5] Tietz, N. W. Fundamentals of Clinical Chemistry, 2nd ed., W. B. Saunders Co., Philadelphia, PA, 994-999 (1976).
[6] Baselt, R. C. Biological Monitoring Methods for Industrial Chemicals, Biomedical Publications, Davis, CA, 140-143 (1980).
[7] Lauwerys, R. R. Industrial Chemical Exposure: Guidelines for Biological Monitoring, Biomedical Publications, Davis, CA, 26-27, 134 (1983).

METHOD WRITTEN BY: Larry K. Lowry, Ph.D. and William P. Tolos, NIOSH/DBBS.

FORMULA: $C_6H_5CONHCH_2COOH$;
$C_9H_9NO_3$

HIPPURIC ACID in urine

METHOD: 8300
ISSUED: 2/15/84

M.W.: 179.18

BIOLOGICAL INDICATOR OF: exposure to toluene.

SYNONYMS: N-benzoylglycine ; CAS # 495-69-2

BIOLOGICAL SAMPLING	MEASUREMENT
SPECIMEN: urine, end of shift after 2 days exposure	TECHNIQUE: VISIBLE ABSORPTION SPECTROPHOTOMETRY
VOLUME: 50 to 100 mL in 125-mL plastic bottle	ANALYTE: colored complex of hippuric acid and benzenesulfonyl chloride
PRESERVATIVE: a few crystals of thymol; keep at about 4 °C	WAVELENGTH: 410 nm
SHIPMENT: pack in insulated shipper with bagged refrigerant; ship by air express	PATH LENGTH: 1 cm
STABILITY: stable 1 day @ 20 °C; 1 week @ 4 °C; and 2 months @ -20 °C	CALIBRATION: aqueous hippuric acid standards
CONTROLS: collect pre-shift urines as well as urines from non-exposed controls	QUALITY CONTROL: frozen pooled urine; correct for creatinine content
	RANGE: 0.005 to 0.5 g/L (1:5 urine dilution)
	ESTIMATED LOD: 0.002 g/L
	PRECISION (s_r): 0.06

APPLICABILITY: Toluene is metabolized by the body and is excreted in the urine as hippuric acid, the glycine congugate of benzoic acid. This method is useful in screening workers exposed to toluene in the absence of xylene or styrene. The latter 2 compounds produce metabolites that are measured as "hippuric acid."

INTERFERENCES: In addition to positive interferences from styrene and xylene in the workplace, the ingestion of salicylic acid or aspirin by the worker will produce a positive interference. A careful work history/questionnaire is suggested.

OTHER METHODS: This method replaces P&CAM 327 [1] with minor revisions. Method 8301 is a specific HPLC method and can be used in the presence of xylene, styrene, salicylic acid and aspirin. Other biological monitoring methods include measurement of blood toluene and alveolar air toluene [2].

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REAGENTS:

1. Calibration stock solution, 0.5 g/L. Dissolve 50 mg hippuric acid in 100 mL distilled water Stable one month at 25 °C.
2. Benzensulfonyl chloride.*
3. Pyridine, reagent.*
4. Thymol, USP.
5. Ethanol, absolute.

*See Special Precautions.

EQUIPMENT:

1. Bottles, polyethylene, 125-mL.
2. Spectrophotometer, 1-cm light path, to read at 410 nm, band width ≤ 10 nm, with 1-cm cuvettes.
3. Centrifuge, clinical, table top.
4. Centrifuge tubes, 15-mL, conical.
5. Pipets, serological, 0.5-, 1.0-, and 5.0-mL
6. Pipet bulb.
7. Mixer, vibration.
8. Volumetric flasks, 10- and 100-mL.
9. Graduated cylinder, 10-mL.

SPECIAL PRECAUTIONS: Work with pyridine and benzenesulfonyl chloride only in a fume hood.

SAMPLING:

1. Collect a spot urine sample of 50 to 100 mL in a 125-mL polyethylene bottle containing a few crystals of thymol.
   NOTE: Take the sample at the end of the second day of suspected exposure to toluene. Also take pre-exposure samples and samples from non-exposed workers as controls.
2. Pack the samples in an insulated shipper with bagged refrigerant.

SAMPLE PREPARATION:

3. Thaw the urine samples, if frozen.
4. Perform a creatinine determination on an aliquot of the urine (e.g., [3]).
5. Dilute 1 volume urine with 4 volumes distilled water.

CALIBRATION AND QUALITY CONTROL:

6. Prepare working standards over the range of 0.005 to 0.5 g/L by dilution of calibration stock solution. Working standards are stable for one week at room temperature.
7. Analyze the working standards (steps 10 through 15).
8. Include a frozen pooled urine control with each measurement run.
9. Plot the absorbance at 410 nm against hippuric acid concentration (g/L) in the working standard to prepare the calibration graph.

MEASUREMENT:

10. Mix 0.5 mL diluted urine and 0.5 mL pyridine in a conical centrifuge tube.
11. Add 0.2 mL benzenesulfonyl chloride and mix for about 5 sec on a vibration mixer.
12. Let stand for 30 min at 20 to 30 °C.
13. Stop the reaction by adding 5.0 mL ethanol, followed by mixing on a vibration mixer.
14. Centrifuge at 1500 to 2000 RPM (full speed) for 5 min to reduce turbidity.
15. Remove supernatant with pipet and place in a 1-cm cuvette. Read absorbance at 410 nm using ethanol to zero the instrument.
    NOTE: If absorbance is above the calibration range, discard the sample and start a new sample (beginning at step 5) with greater dilution.

CALCULATIONS:

16. Determine the concentration, C_s (g/L), of hippuric acid corresponding to the absorbance of the sample from the calibration graph.
17. Calculate the concentration of hippuric acid/g creatinine in the urine sample, C (g/g creatinine), using the dilution factor, D (usually 5), from step 5 and the creatinine value, C_r (g creatinine/L urine), from step 4:

$$C = \frac{C_s \times D}{C_r}, \text{ g hippuric acid/g creatinine.}$$

GUIDES TO INTERPRETATION:

1. Tomukuni, et al. [4] reported a normal range in 20 non-exposed adults as 0.44 ± 0.20 g/L (equivalent to approximately 0.7 g/g creatinine).
2. Lauwerys [2] reported a normal range of 1.5 g/g creatinine and a "tentative maximum permissible value" of 2.5 g/g creatinine.
3. Pagnotto, et al. [5] reported that exposure to 100 ppm toluene would produce end-of-shift urinary hippuric acid levels of 4 g/L (equivalent to about 5 g/g creatinine).
4. Urine from non-exposed workers should be collected, as well as pre-shift specimens from exposed workers because levels of hippuric acid in urine vary widely.

EVALUATION OF METHOD:

Precision (s_r) for within-run and day-to-day runs over the analytical range was found to average 0.06. No method comparison studies have been conducted.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd Ed., Vol. 6, Method P&CAM 327, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).
[2] Lauwerys, R.R. Industrial Chemical Exposure: Guidelines for Biological Monitoring, Biomedical Publications, Davis, California, 57-65 (1983).
[3] Tietz, N.W. Fundamentals of Clinical Chemistry, 2nd ed., 994-999, W.B. Saunders Co., Philadelphia, PA (1976).
[4] Tomokuni, K. and M. Ogata. Direct Colorimetric Determination of Hippuric Acid in Urine, Clin. Chem. 18, 349-351 (1972).
[5] Pagnotto, L.D. and L.M. Lieberman. Am. Ind. Hyg. Assoc. J., 28, 129-134 (1967).

METHOD WRITTEN BY: Larry K. Lowry, Ph.D., NIOSH/DBBS.

(1) HIPPURIC and METHYL HIPPURIC ACIDS in urine

FORMULA: (1) $C_2H_5CONHCH_2CO_2H$
(2) $CH_3C_6H_4CONHCH_2CO_2H$
M.W.: (1) 179.17; (2) 193.2

METHOD: 8301
ISSUED: 2/15/84

BIOLOGICAL INDICATOR OF: exposure to toluene and xylene.

SYNONYMS: (1) N-benzoylglycine ; CAS # 495-69-2

BIOLOGICAL SAMPLING	MEASUREMENT
SPECIMEN: urine, end of shift after 2 days exposure	TECHNIQUE: HPLC-UV DETECTION
VOLUME: complete spot voiding	ANALYTE: hippuric acid and methyl hippuric acid
PRESERVATIVE: a few crystals of thymol; keep @ 4 °C	EXTRACTANT: ethyl acetate
SHIPMENT: pack in styrofoam shipper with "bag ice"; ship by air express	WAVELENGTH: 254 nm
STABILITY: stable for 1 week @ 4 °C and 2 months @ -20 °C	COLUMN: reverse phase (C_{18})
CONTROLS: collect samples from unexposed, matched population as well as pre-shift urines from exposed workers	MOBILE PHASE: 90/10/0.02% (v/v) water/acetonitrile/glacial acetic acid; 3 mL/min
	CALIBRATION: aqueous solutions of analyte
	QUALITY CONTROL: frozen pooled urine; normalize to creatinine
	RANGE: 0.2 to 1.0 mg/mL
	ESTIMATED LOD: (1) 0.015 µg/mL; (2) 0.030 µg/mL
	RECOVERY: 98%
	PRECISION (s_r): 0.04

APPLICABILITY: Hippuric acid and m-methyl hippuric acid are the principle metabolites of toluene and xylene, respectively. An occupational exposure to either of these organic solvents may be monitored by following the pattern of excretion of these metabolites in urine.

INTERFERENCES: None known; however, para and meta isomers elute together in this system. There are other sources of hippuric acid such as food preservatives, ethylbenzene, and styrene.

OTHER METHODS: This is a new method based on reference [1]. Method 8300 can be used for screening. Isotachophoresis has also been used [2].

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REAGENTS:

1. Thymol, USP.
2. Sodium chloride.
3. Hydrochloric acid, conc. (36% w/w).
4. Ethyl acetate, HPLC quality.
5. Hippuric acid stock solution, 1 mg/mL. Dissolve 100.0 mg hippuric acid in 75 mL distilled water. Dilute to 100 mL. Stable 1 month.
6. o-Methyl hippuric acid, 1 mg/mL. Prepare as described for hippuric acid.
7. m-Methyl hippuric acid, 1 mg/mL. Prepare as described for hippuric acid.
8. p-Methyl hippuric acid, 1 mg/mL. Prepare as described for hippuric acid.
9. Mobile phase. Add 900 mL distilled water to 100 mL acetonitrile (HPLC grade) and 200 µL glacial acetic acid. Mix and filter.
10. Prepurified nitrogen, 99.9%.

EQUIPMENT:

1. Bottles, polyethylene, 250-mL.
2. HPLC system consisting of sample injector, pump, column, ultraviolet detector at 254 nm, strip chart recorder, integrator, and column; plastic, 14 x 155 mm, packed with 10 µm irregularly-shaped reversed phase (C_{18}) packing.
3. Radial compression module capable of delivering constant, uniform pressure to the entire longitudinal surface of the column.
4. Concentrator-evaporator with heated waterbath.
5. Centrifuge.
6. Analytical balance.
7. Pipettes, serological, 10-mL, with pipet bulb.
8. Centrifuge tubes, glass-stoppered, graduated, 15-mL.
9. Culture tubes, 12 mm x 75 mm, disposable.
10. Micropipettes, 40-, 100- and 200-µL.
11. Microsyringe, 10-µL.

SPECIAL PRECAUTIONS: None.

SAMPLING:

1. Collect a spot sample of urine in a 250-mL polyethylene bottle containing a few crystals of thymol.
   NOTE: Take the sample at the end of the second day of suspected exposure to toluene or xylene. Also take pre-exposure samples and samples from non-exposed workers as controls.
2. Pack bottles in styrofoam shipper with "bag ice" and ship by air express.

SAMPLE PREPARATION:

3. Perform a creatinine determination on an aliquot of urine (e.g., [3]).
4. Pipette 1.0 mL of well-mixed urine into a 15-mL graduated centrifuge tube.
5. Add 40 µL conc. HCl, mix, and add 0.3 g sodium chloride (enough to saturate).
6. Add 4 mL ethyl acetate. Shake for 2 min.
7. Centrifuge at 100 xgravity for 5 min. Transfer 200 µL of the organic layer to a culture tube and evaporate to dryness using a heated waterbath and a gentle stream of nitrogen.
8. Redissolve the residue in 200 µL distilled water.

CALIBRATION AND QUALITY CONTROL:

9. Prepare working standards over the range 0.2 to 1 mg/mL by dilution of hippuric acid stock solution and methyl hippuric acid stock solutions with distilled water. Working standards are stable for 1 week at room temperature.
10. Prepare and analyze the working standards together with samples, blanks and controls (steps 4 through 8 and 14 and 15).

11. Determine the peak height to concentration ratio (H/C) using the mean peak height of three injections for each working standard. Calculate the response factor, F, for each compound by dividing the respective peak height to concentration ratio by the peak height to concentration ratio for hippuric acid.
12. Include a batch of replicate standards with each batch of samples.
13. Include aliquots of previously analyzed frozen urine pool.

MEASUREMENT:

14. Set up the HPLC according to manufacturer's recommendations and to conditions on page 8301-1.
15. Inject 5 µL of the test solution from step 8 into the HPLC. Determine peak heights.

CALCULATIONS:

16. Calculate the concentration of analyte in the urine sample, C_U (mg/mL), using the concentration of a standard, C_S (mg/mL), the peak height of the analyte, H, and the peak height of the respective standard, H_S:

$$C_U = \frac{C_S \times H}{F \times H_S}.$$

17. Calculate the concentration of analyte/g creatinine in the urine sample, C (g/g creatinine), using the concentration of creatinine in urine determined in step 3, C_r (g creatinine/L urine):

$$C = \frac{C_U}{C_r}.$$

GUIDES TO INTERPRETATION:

1. The upper limit of the range for hippuric acid in non-exposed NIOSH employees was 0.6 mg/mL (0.6 g/L). M-methyl hippuric acid is not found in non-exposed humans.
2. Lauwerys [4] reports an upper limit of normal for hippuric acid of 1.5 g/g creatinine using a specific gas chromatographic method. He reports a "tentative maximum permissible value" of 2.5 g/g creatinine.
3. Lauwerys [4] reports a "tentative maximum permissible value" of 1.5 g/g creatinine for methyl hippuric acid collected at the end of a work shift.

EVALUATION OF METHOD:

Within-run precision (s_r) averaged 0.04 over the analytical range. No further evaluation of the method was performed except as reported by Matsui, et al. [1].

REFERENCES:

[1] Matsui, H., M. Kasao, and S. Imamura. High Performance Liquid Chromatographic Determination of Hippuric Acid in Human Urine, J. Chromatog., 45, 231 (1978).

[2] Sollenberg, J. and A. Baldesten. Isotachophoretic Analysis of Mandelic Acid, Phenylglyoxylic Acid, Hippuric Acid and Methyl Hippuric Acid in Urine After Occupational Exposure to Styrene, Toluene and/or Xylene, J. Chromatog., 132, 469 (1977).

[3] Tietz, N.W. Fundamentals of Clinical Chemistry, 2nd ed., pp. 994-999, W.B. Saunders Co., Philadelphia, PA (1976).

[4] Lauwerys, R.R. Industrial Chemical Exposure: Guidelines for Biological Monitoring, Biomedical Publications, Davis, CA, 57-69 (1983).

METHOD WRITTEN BY: Frederick C. Phipps, NIOSH/DBBS.

FORMULA: Pb

LEAD IN BLOOD AND URINE

METHOD: 8003

M.W.: 207.19

ISSUED: 2/15/84

BIOLOGICAL INDICATOR OF: exposure to lead and lead compounds.

SYNONYMS: none.

BIOLOGICAL SAMPLING	MEASUREMENT
SPECIMEN: whole blood; urine, end of shift	TECHNIQUE: ATOMIC ABSORPTION, AIR/ACETYLENE
CONTAINER: 10-mL lead-free tubes (blood); 125-mL polyethylene bottles (urine)	ANALYTE: Pb(II)-APDC complex
	EXTRACTION: APDC- MIBK
ANTICOAGULANT: (blood) heparin	CALIBRATION: methyl isobutyl ketone solutions of Pb(II)-APDC complex
PRESERVATIVE: (urine) 0.2 mL conc. HNO_3	
SHIPMENT: polyethylene shippers	QUALITY CONTROL: commercial controls; pooled urine or blood; urine corrected for creatinine
STABILITY: blood stable 3 days @ 4 °C; indefinitely if sonicated and frozen in plastic tubes; urine stable indefinitely if kept acidified with HNO_3	RANGE: 5 to 150 µg/100 g blood; 5 to 150 µg/100 mL urine
	ESTIMATED LOD: 0.05 µg Pb/g blood or mL urine
CONTROLS: commercial urine and blood lead control samples plus pooled urine and blood from non-exposed populations	RECOVERY: 0.99
	PRECISION (s_r): 0.05

APPLICABILITY: This procedure quantitates Pb^{+2} in blood or urine to assess body burden, injury to the hematopoietic system, and to comply with Federal Regulations. Blood lead is the preferred biological indicator of lead absorption. The optimum working range is 0.1 to 1.5 µg Pb per g blood or per mL urine [7].

INTERFERENCES: Phosphate, EDTA, and oxalate can sequester lead and cause low lead readings.

OTHER METHODS: This method combines and replaces P&CAM 208 and 262 [6]. Methods P&CAM 102 (dithizone), 195 (ASV), 200 (ASV) and 214 (graphite furnace AAS) [6] have not been revised. Anodic stripping voltametry (ASV) is an alternative procedure if specialized equipment is available [1].

REAGENTS:

1. Ammonium pyrrolidine dithiocarbamate (APDC). Stable 6 months.
2. Nonionic surfactant, octyl phenoxy polyethoxy ethanol (Triton X-100 or equivalent).
3. APDC-surfactant solution (APDC-Tx). Dissolve 4 g APDC and 5 mL nonionic surfactant in 40 mL deionized water. Dilute to 200 mL. Check each batch for extraction efficiency. Stable at least two months.
4. Lead nitrate $(Pb)(NO_3)_2$. Heat 4 hrs at 120 °C. Cool and store in dessicator.
5. Nitric acid, conc. 70% (w/w), redistilled.
6. Methyl isobutyl ketone (MIBK), water-saturated. Add 100 mL water to 900 mL MIBK. Shake and allow to stand 1 hr.
7. Calibration stock solution (1000 µg/mL). Dissolve 1.598 g $Pb(NO_3)_2$ in 2% (w/v) HNO_3 and dilute to 1 L. Store in a polyethylene bottle. Stable 1 year.
8. Air at 40 psi, filtered to remove oil and water.
9. Acetylene, grade recommended by AA manufacturers.

EQUIPMENT:

1. Heparinized, lead-free, "blue-top" blood collection tubes specially prepared for collecting blood samples for blood lead determinations.
2. Vacutainer needles (21-gauge) and holder.
3. Tourniquet and alcohol swabs.
4. Polyethylene bottles (wide mouth), 125-mL.
5. Culture tubes, 16 x 100 mm, with PTFE-lined screw caps.*
6. Centrifuge.
7. Rotary vibration mixer (Vortex) or equivalent.
8. Atomic absorption spectrophotometer (AA) with lead hollow cathode or electrodeless discharge lamp.
9. Analytical balance.
10. Desiccator.
11. Pipettes, volumetric flasks and other appropriate glass or plasticware for weighing, storing, and dispensing reagents and samples.*

*All glassware and plasticware should be detergent washed, thoroughly rinsed with tap and deionized water, soaked 4 hrs in 1:1 HNO_3:H_2O and finally thoroughly rinsed with deionized water.

SPECIAL PRECAUTIONS: None.

SAMPLING:

1. Collect blood samples in heparinized blood collection tubes. Mix immediately. Ship at 4 °C and maintain at this temperature prior to analysis.
2. Collect urine at the end of a work shift in 125-mL polyethylene bottles containing 0.2 mL conc. HNO_3; mix. Submit a 25-mL aliquot for lead analysis and another 25-mL aliquot for creatinine determination.

SAMPLE PREPARATION:

3. Filter urine samples before analysis. Analyze a 25-mL aliquot for creatinine by standard procedures (e.g., [2]).
4. Add 2.0 mL filtered urine or 2.00 g whole blood into a 16 x 100 mm culture tube. Start a reagent blank at this point with 2 mL deionized water.
5. Add 0.8 mL APDC-surfactant solution. Cap and mix on a rotary vibration mixer for 10 sec.
6. Add 2.00 mL water-saturated MIBK. Cap and rotate on a rotary vibration mixer for 2 min. Centrifuge at 2000 rpm for 10 min. Analyze the Pb-APDC solution in MIBK within 2 hrs of extraction.

NOTE: If the patient is receiving EDTA therapy or if blood specimens are collected in tubes containing Na_2 EDTA as anticoagulant, add 0.05 mL 1.5 M $CaCl_2$ immediately before adding the MIBK [3].

CALIBRATION AND QUALITY CONTROL:

7. Prepare 6 working standards in deionized water in the range 10 to 150 µg Pb/100 mL by dilution of calibration stock solution with 2% (w/v) HNO_3. Prepare fresh daily.
   Example: 0.4 mL calibration stock stolution diluted to 1 L = 40 µg per 100 mL.
8. Analyze the working standards (steps 4, 5, 6, 12, and 13).
9. Prepare a calibration graph. Plot concentration (µg/100 mL) vs. absorbance of working standard, corrected for reagent blank.
10. Maintain standardization by analyzing a standard after every 5 samples.
11. Run a spiked control or pooled sample from exposed workers or commercial control every 10 samples or at least 3 per study.
    NOTE: Blood or urine lead background levels must be determined before spiked controls are prepared.

MEASUREMENT:

12. Set up the atomic absorption spectrophotometer and lamp conditions as recommended by the manufacturer and as given on page 8003-1. Aspirate water-saturated MIBK and reduce acetylene flow until a stoichiometric flame with minimum background is obtained (< 0.01 absorbance). Record this reading.
13. Aspirate each sample and blank. Record maximum absorbances.
    NOTE: Samples with absorbance values greater than 0.35 must be diluted with MIBK and reanalyzed. Apply the appropriate dilution factor in calculations.

CALCULATIONS:

14. Calculate net absorbance (difference between the maximum absorbance of MIBK and the absorbance of the sample or blank).
15. Calculate blood and urine lead levels by comparing the net sample absorbance minus net absorbance for reagent blanks with the calibration graph.
16. For urine samples, report µg/Pb/g of creatinine.

GUIDES TO INTERPRETATION:

Blood lead concentrations for healthy adult suburbanites is 7 to 22 µg/100 g whole blood [4]. Urine has a wider range, 4 to 270 µg/g creatinine, for the same population; however, most normal values should be near 16 to 60 µg/g creatinine [4].

Blood lead values are commonly used for biological monitoring. A blood lead value above 40 µg/100 g is indicative of excess exposure and one above 60 µg/100 g requires removal from exposure [5].

EVALUATION OF METHOD:

Forty-two blood specimens were spiked at levels of 25 to 200 µg/100 mL. Recoveries were 94 to 106%, averaging 100% [3].

For urine, 25 specimens were spiked at concentrations from 10 to 100 µg/mL. Recoveries averaged 100% (range 95 to 106%) [3].

REFERENCES:
[1] Environmental Sciences Associates, Inc. Methods Manual Methods TMA-1 and TMA-2, Bedford, MA.
[2] Tietz, N. W. Fundamentals of Clinical Chemistry, 2nd ed., 994-999, W. B. Saunders Co., Philadelphia, PA (1976).
[3] Zenterhofer, L. J. M., P. I. Jatlow, and A. Fappiano. Atomic Abosrption Determination of Lead in Blood and Urine in the Presence of EDTA, J. Lab. Clin. Med., 78, 664-674 (October, 1971).
[4] Baselt, R. C. Biological Monitoring Methods for Industrial Chemicals, 159, Biomedical Publications, Davis, CA (1980).
[5] Occupational Safety and Health Administration, Chapter XVII, 1910.1025, Section C, 691.
[6] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[7] Hessel, D. W. Atomic Absorption Newslett., 7, 55 (1968).

METHOD WRITTEN BY: Anthony W. Smallwood and Frederick C. Phipps, NIOSH/DBBS;
Peter M. Eller, Ph.D., CIH, and Mark B. Millson, NIOSH/DPSE.

FORMULA: $(H_2NC_6H_3Cl)_2CH_2$;
$C_{13}H_{12}N_2Cl_2$

M.W.: 267.16

MBOCA IN URINE

METHOD: 8302
ISSUED: 2/15/84

BIOLOGICAL INDICATOR OF: exposure to 4,4'-methylenebis (2-chloroaniline).

SYNONYMS: MOCA; di-(4-amino-3-chlorophenyl) methane; 4,4'-methylenebis (2-chloroaniline); CAS #101-14-4.

BIOLOGICAL SAMPLING	MEASUREMENT
SPECIMEN: 2 urines (pre- and post-exposure)	TECHNIQUE: GAS CHROMATOGRAPHY, ECD
VOLUME: 50 to 100 mL in polyethylene screw-cap bottle containing preservative	ANALYTE: pentafluoropropionyl MBOCA derivative
PRESERVATIVE: 3 mL of 30% (w/w) citric acid solution	EXTRACTIONS: MBOCA and derivative
SHIPMENT: freeze urine and ship in dry ice in an insulated container	INJECTION VOLUME: 5 µL
STABILITY: stable for 2 days @ 25 °C and for 1 month @ -20 °C	TEMPERATURE-INJECTOR: 250 °C -DETECTOR: 300 °C -COLUMN: 220 °C
CONTROLS: collect urine from non-exposed workers	COLUMN: 3 m x 2 mm ID glass, 3% OV-1 on 100/120 mesh Gas Chrom Q
	CARRIER GAS: 5% methane in argon, 40 mL/min
	CALIBRATION: control urine spiked with MBOCA; MDA as internal standard
	QUALITY CONTROL: frozen pooled urine; correct for creatinine content
	RANGE: 10 to 250 µg/L urine
	ESTIMATED LOD: 1 µg/L urine
	RECOVERY: 89% (100 µg/L of urine); 79% (4 to 25 µg/L urine)
	PRECISION (s_r): 0.08

APPLICABILITY: MBOCA is commonly found in the urine of humans exposed to the compound in the plastic industry. Despite the extensive metabolism of MBOCA in the rat, analysis of the urine of exposed workers showed only MBOCA [1]. This GC-ECD method is useful in screening workers exposed to MBOCA.

INTERFERENCES: Imipramine has a similar retention time. A careful work history/questionnaire is suggested.

OTHER METHODS: This method replaces P&CAM 342 [2] with minor revisions. This method is 40-fold more sensitive than the method in the Special Hazard Review [3]. A similar, less sensitive method using GC-FID has been described [4].

REAGENTS:

1. 4,4'-Methylenebis (2-chloroaniline) (MBOCA) stock standard, 200 µg/mL.* Accurately weigh 50 mg MBOCA. Dissolve in a small volume of methanol. Dilute to 250 mL with methanol. Stable five days at 25 °C.
2. 4,4'-Methylenedianiline (MDA), internal standard, 10 µg/mL in methanol.
3. Hexane.
4. Diethyl ether.
5. Triethylamine (TEA), 0.05 M stock solution in hexane.
6. Pentafluoropropionic anhydride (PFPA).
7. Florisil, 60 to 100 mesh, activated by the manufacturer at 650 °C, heated to 130 °C for 24 hrs, and then deactivated by adding 10% (w/w) water and mixing 2 hrs on a rotary mixer at 50 rpm. Stable one week.
8. Benzene.
9. NaOH.
10. KH_2PO_4, 0.1 M, adjusted to pH 6 with conc. HCl.
11. Sodium sulfate, granular, anhydrous.
12. Methanol.
13. Citric acid, monohydrate, granular.
14. Pooled urine sample or Hycel urine control (Hycel Co., Houston, TX).
15. HCl, conc.
16. P-5 carrier gas, 5% methane in argon.

*See Special Precautions.

EQUIPMENT:

1. Bottles, polyethylene, screw-top, 125-mL.
2. Gas chromatograph with ^{63}Ni electron capture detector.
3. Integrator, mechanical or electronic for determining GC peak areas.
4. GC glass column, 3 m x 2 mm ID, packed with 3% OV-1 on 100/120 mesh Gas Chrom Q.
5. Pipets, Pasteur.
6. Centrifuge tubes, 15-mL, graduated, glass-stoppered.
7. Mixer, rotary, 50 to 60 rpm, for 20-mm culture tubes.
8. Culture tubes, 20 x 150 mm, screw-cap, PTFE-lined.
9. Mixer, vibration.
10. Chromatography column, 7-mm ID x 20-cm, with a 25-mL reservoir and Teflon stopcock.
11. pH paper, wide range.
12. Nitrogen manifold for evaporating organic solutions.
13. Pipets, 10-mL.
14. Centrifuge, table top, clinical.
15. Syringes, glass, 10- and 50-µL.
16. Waterbath, 50 °C.
17. Volumetric flasks, 100- and 250-mL.
18. Glass wool.

SPECIAL PRECAUTIONS: MBOCA and benzene are suspect carcinogens; handle either in a glove box or a well-ventilated hood.

Handle ethyl ether and hexane with care; both are highly flammable and should be used in a hood.

SAMPLING:

1. Collect 50 to 100 mL urine in a 125-mL polyethylene bottle containing 3 mL 30% citric acid.
2. Close the polyethylene bottle immediately after sample collection and swirl gently to mix.
3. Freeze the urine and ship in dry ice in an insulated container.

SAMPLE PREPARATION:

4. Defrost urine sample.
5. Perform a creatinine determination on an aliquot of the urine (e.g., [5]).
6. Adjust the urine pH to 1 with HCl.
7. Pipet a 10-mL aliquot of urine into a clean culture tube.
8. Adjust the pH to 10 using 10 N NaOH (approximately 0.1 mL).
9. Add 3 mL of methanol. Mix well.
10. Add 5 mL of 1:1 diethyl ether:hexane and shake steadily for 2 min to extract the MBOCA. Centrifuge to separate phases and transfer the organic phase with the aid of a Pasteur pipet to a culture tube. Repeat with 2 additional 5-mL portions of 1:1 diethyl ether:hexane, combining the organic phases.
    NOTE: Emulsions may form; break them by adding methanol or by repeated centrifugation.
11. Concentrate the extract to approximately 1 mL under a gentle stream of nitrogen in a hood.
12. Add 50 µL of TEA, 50 µL of PFPA and 10 µL of MDA to the concentrated extract. Mix well in a hood.
13. Secure the cap loosely. Heat in a waterbath at 50 °C for 15 min.
14. Remove from waterbath. Add 2 mL hexane and 5 mL of pH 6 KH_2PO_4 buffer. Mix well.
15. Centrifuge to separate the organic and aqueous phases completely. Transfer the organic layer containing the derivative, without disturbing the aqueous phase, with a Pasteur pipet into a 15-mL centrifuge tube.
16. Add 2 mL hexane to the aqueous buffer and mix well. Repeat step 15. Transfer the organic layer to the same 15-mL centrifuge tube. If low exposure is expected, less than 30 µg/L urine, use Florisil cleanup (see APPENDIX). Dilute the organic solution to 5 mL with hexane; add 0.2 g Na_2SO_4 and mix.

CALIBRATION AND QUALITY CONTROL:

17. Prepare working standards over the range from 0 to 200 µg/L urine by adding stock standard MBOCA to a control urine.
18. Extract 10 mL of each working standard (steps 7 through 16).
19. Plot MBOCA concentration (µg/L urine) vs. the ratio, R, of the peak area of MBOCA in the working standards to the peak area of MDA in the same working standard to prepare the calibration graph.
20. Include a frozen pooled urine control with each analytical run.
21. Set the gas chromatograph according to manufacturer's recommendations and the conditions on page 8302-1.

MEASUREMENT:

22. Inject 5 µL of the hexane extract from step 16.
23. Measure the peak areas of the samples and internal standard.

CALCULATIONS:

24. Divide the peak area of the sample by the peak area of the internal standard on the same chromatogram to calculate R for the sample.
25. Determine the MBOCA concentration in the urine sample, C_u (µg/L), from the calibration graph.
26. Calculate the concentration of MBOCA/g creatinine in the urine sample, C (µg/g creatinine), using the creatinine value obtained in step 6.

$$C = \frac{C_u}{C_r}, \text{ µg MBOCA/g creatinine.}$$

GUIDES TO INTERPRETATION:
Linch, et al. [1] reported exposed workers having MBOCA at concentrations up to 370 µg/L of urine. No other reports have been found in the literature.

EVALUATION OF METHOD:
Spiked urine specimens containing MBOCA concentrations of 4, 30 and 150 µg/L urine were analyzed in groups of 10 for each concentration. Precision (s_r) over the above analytical range was found to be 0.08.

REFERENCES:
[1] Linch, A.L., O'Connor, G.B., Barnes, J.R., Killian, A.S. and Neeld, W.E. Methylene-bis-Ortho-Chloroaniline (MOCA®): Evaluation of Hazards and Exposure Control. Am. Ind. Hyg. Assoc. J., 32, 802-819 (1971).
[2] NIOSH Manual of Analytical Methods, V. 7, Method P&CAM 342, U.S. Department of Health and Human Services, Publ. (NIOSH) 82-100 (1981).
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[5] Tietz, N.W. Fundamentals of Clinical Chemistry, 2nd ed., 994-999, W.B. Saunders, Co., Philadelphia, PA (1976).

METHOD WRITTEN BY: William P. Tolos, NIOSH/DBBS.

APPENDIX:

FLORISIL CLEANUP AND ANALYSIS (for MBOCA less than 30 µg/L urine)
1. Concentrate the extract (step 15) to approximately 0.5 mL under a gentle stream of nitrogen at 30 °C in a waterbath.
2. Place a small glass wool plug in a chromatographic column. Add 1.6 g of 10% deactivated Florisil. Top with 2 cm of anhydrous Na_2SO_4.
3. Pre-rinse the packed column with 10 mL of hexane.
4. Transfer the 0.5 mL of derivatized extract to the column with a Pasteur pipet. Add the extract just as the level of hexane rinse is even with the Na_2SO_4 layer.
5. Quickly rinse the extract tube with several additional small quantities of hexane. Do not allow the level of rinse to fall below the Na_2SO_4 layer.
6. Discard the eluted pre-rinse.
7. Elute the column with 10 mL of 40% benzene/hexane (v/v). The solvent mixture should not fall below the Na_2SO_4 layer; discard the eluate.
8. Elute the column with 10 mL of 100% benzene. Save the eluate and concentrate to 1 mL.
9. Inject 2 µL of the concentrated benzene fraction into the GC that has been set to the conditions described on page 8302-1, except increase the injection temperature to 240 °C. Retention time is about 5 min.

FORMULA: Table 1

M.W.: Table I

METALS in urine

METHOD: 8310
ISSUED: 2/15/84

BIOLOGICAL INDICATOR OF: exposure to the following metals or their compounds: aluminum, barium, cadmium, chromium, copper, iron, lead, manganese, molybdenum, nickel, platinum, silver, strontium, tin, titanium, and zinc.

SYNONYMS: vary according to the compound.

BIOLOGICAL SAMPLING	MEASUREMENT
SPECIMEN: urine	TECHNIQUE: INDUCTIVELY-COUPLED ARGON PLASMA, ATOMIC EMISSION SPECTROSCOPY
VOLUME: 50 to 200 mL in polyethylene bottle	ANALYTE: elements above
PRESERVATIVE: 5.0 mL conc. HNO_3 added after collection	EXTRACTION MEDIA: polydithiocarbamate resin
SHIPMENT: frozen in dry ice	FINAL SOLUTION: 4% HNO_3, 1% $HClO_4$; 5 mL
STABILITY: not established	WAVELENGTH: depends upon element; Table 1
CONTROLS: collect at least 3 urine specimens from unexposed workers	BACKGROUND CORRECTION: spectral wavelength shift
	CALIBRATION: elements in 4% HNO_3, 1% $HClO_4$
	QUALITY CONTROL: spiked urines; corrected for creatinine
	RANGE: 0.25 to 200 µg per sample [1]
	ESTIMATED LOD: 0.1 µg per sample
	PRECISION (s_r): Table 1

APPLICABILITY: This method measures urine concentrations of metals. It is particularly useful for workers exposed to several metals simultaneously. This is a simultaneous, multielemental analysis, but is not compound specific.

INTERFERENCES: Spectral interferences are the primary interferences encountered in ICP-AES analysis. These are minimized by judicious wavelength selection and interelement correction factors. Background corrections are also made [1,2].

OTHER METHODS: This is a new method which uses a measurement technique similar to that of Method 7300 for air samples.

REAGENTS:

1. Polydithiocarbamate resin, prepared as described in the APPENDIX.
2. Nitric acid, conc.*
3. Perchloric acid, conc.*
4. Dissolution acid, 4:1 (v/v) HNO_3:$HClO_4$. Mix 4 volumes conc. HNO_3 with 1 volume conc. $HClO_4$.*
5. Metals standards, 1000 µg/mL. Commercially available or prepared per instrument manufacturer's recommendations.
6. Argon.
7. Deionized water.
8. Sodium hydroxide, 5 M. Dissolve 20 g NaOH in 50 mL boiled, deionized water; dilute to 100 mL. Store in a polyethylene bottle.

*See Special Precautions.

EQUIPMENT:

1. Bottles, polyethylene, 125- or 250-mL, plastic-lined screw-cap.*
2. Inductively-coupled plasma-atomic emission spectrometer equipped for determination of elements of interest.
3. Regulator, two-stage, for argon.
4. Filtering apparatus for 50 mL liquid with 47-mm cellulose ester, 0.8-µm pore size filters.
5. Beakers, Griffin, 50-mL, with watchglass covers.*
6. pH meter and electrodes.
7. Volumetric flasks, 5- and 100-mL.*
8. Assorted volumetric pipets as needed.*
9. Hotplate, suitable for use at 100 °C.
10. Mechanical shaker.
11. Low temperature oxygen plasma asher (acid ashing may be substituted; see APPENDIX).

*Clean all labware with detergent, soak 12 hrs in 10% (v/v) HNO_3, and soak 12 hrs in deionized water.

SPECIAL PRECAUTIONS: Concentrated acids are extremely corrosive. Work with concentrated acids only in fume hoods and wear appropriate safety equipment (safety glasses or face shield, gloves, and labcoat).

SAMPLING:

1. Collect a 50-mL urine sample in a polyethylene bottle.
2. Add 5 mL conc. HNO_3 as a preservative.
3. Pack samples in an insulated shipping container under refrigeration (e.g., styrofoam with dry ice) for transportation to laboratory.

SAMPLE PREPARATION:

4. Perform a creatinine determination on an aliquot of the sample (e.g., [5]).
5. Adjust the sample pH to 2.0 ± 0.1 with 5 M NaOH and then add 60 ± 10 mg polydithiocarbamate resin.
   NOTE: Start reagent blanks, in triplicate, at this step. Include resin and filters (step 7).
6. Agitate samples (on the shaker) for at least 12 hrs.
7. Filter samples through a 0.8-µm cellulose ester membrane filter, saving the filtrate and resin. Place the collected resin and filter in a clean 50-mL beaker.
8. Adjust filtrate pH to 8.0 ± 0.1 with 5 M NaOH, add more resin, then repeat steps 5 and 6, combining the filters and resins from the two extractions.
9. Ash filters and resins in a low temperature oxygen plasma asher for 6 hrs or until ashing is complete (200 watts at 1 to 2 torr, or manufacturer's recommendations).
   NOTE: Steps 5 to 10 of Method 7300 (this Manual), an HNO_3/$HClO_4$ digestion, may be substituted for the low temperature oxygen plasma ashing. Use a final solution volume of 5.0 mL (step 11).

10. Add 0.5 mL dissolution acid and warm on a hotplate (15 min at 50 °C).
11. Transfer solutions quantitatively to 5-mL volumetric flasks and dilute to volume with distilled deionized water.

CALIBRATION AND QUALITY CONTROL:

12. Calibrate the spectrometer according to manufacturer's recommendations.
    NOTE: Typically, an acid blank and 10 µg/mL multielement solutions are used.
13. Analyze a standard for every 10 samples.
14. Check measurement recoveries with at least three spiked unexposed urine samples per 10 samples.
    NOTE: For urine spikes, a 100-mL control urine sample is split and 50 mL analyzed without spiking. The metal quantity found in the unspiked portion is subtracted from the metal quantity found in the spiked portion in order to determine the measurement recovery.

MEASUREMENT:

15. Set the spectrometer to conditions specified by the manufacturer.
16. Analyze standards and samples.
    NOTE: If the values for the samples are above the range of the standards, dilute the sample solutions with 1 volume dissolution acid + 9 volumes deionized water, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

17. Obtain the solution concentration for the sample, C_s (µg/mL), and the average blank, C_b (µg/mL), from the analyses data.
18. Using the solution volumes of sample, V_s (mL), and blank, V_b (mL), calculate the concentration, C (µg/mL), of each element in the volume of urine collected, V (L):

$$C = \frac{(C_s V_s - C_b V_b)}{V}, \ \mu g/L.$$

19. Report the results as µg metal/g creatinine.

GUIDELINES TO INTERPRETATION:

Acceptable and unacceptable levels for metals have not been determined by this method. Lauwerys [6] discusses metals and can be consulted for guidance and interpretation.

EVALUATION OF METHOD:

Recovery of these 16 metals from spiked urine samples are shown in Table 1 (recoveries ranged from 77 to 100%). The precisions determined for the various elements are also given in Table 1 [1].

REFERENCES:

[1] Hull, R. D. and D. Molina. Trace Element Analysis of Urine by Inductively Coupled Plasma-Atomic Emission Spectroscopy, NIOSH Internal Report, NIOSH, DPSE, MRB, IMDS (September, 1983).
[2] Hull, R. D. Multilement Analysis of Industrial Hygiene Samples, NIOSH Internal Report, presented at the American Industrial Hygiene Conference, Portland, OR (May, 1981).
[3] Hackett, D. S. and S. Siggia. Selective Concentration and Determination of Trace Metals Using Polydithiocarbamate Chelating Ion-Exchange Resins, Environmental Analysis, 253, (G. W. Ewing, ed.), Academic Press, NY (1977).

[4] Bray, J. T. and F. J. Reilly. Extraction of Fourteen Elements from a Sea Water Matrix by a Polydithiocarbamate Resin, Jarrell-Ash Plasma Newsletter, 4, 4 (1981).
[5] Tietz, N. W. Fundamentals of Clinical Chemistry, 2nd ed., 994-997, W. B. Saunders Co., Philadelphia, PA (1976).
[6] Lauwerys, R. R. Industrial Chemical Exposure: Guidelines for Biological Monitoring, Biomedical Publications, Davis, CA (1983).

METHOD WRITTEN BY: R. DeLon Hull, NIOSH/DPSE.

Table 1. Recovery of metals from urine [1,2].

Element (Formula)	Atomic Weight	Wavelength (nm)	Metal Quantity Added, µg/50 mL sample	Precision, s_r (n = 4)	% Recovery
Aluminum (Al)	26.98	308.2	20	0.088	100
Barium (Ba)	137.34	455.4	0.4	0.11	80
Cadmium (Cd)	112.40	226.5	1.0	0.12	100
Chromium (Cr)	52.00	205.6	1.0	0.078	100
Copper (Cu)	63.54	324.8	10	0.042	100
Iron (Fe)	55.85	259.9	40	0.059	100
Lead (Pb)	207.19	220.4	10	0.040	100
Manganese (Mn)	54.94	257.6	10	0.50	85
Molybdenum (Mo)	95.94	281.6	2.0	0.16	100
Nickel (Ni)	58.71	231.6	2.0	0.42	80
Platinum (Pt)	195.09	203.7	0.4	0.29	77
Silver (Ag)	107.87	328.3	2.0	0.12	100
Strontium (Sr)	87.62	421.5	4.0	0.25	100
Tin (Sn)	118.69	190.0	2.0	0.21	100
Titanium (Ti)	47.90	334.9	2.0	0.16	86
Zinc (Zn)	65.37	213.9	200	0.089	100

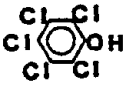
APPENDIX:

POLYDITHIOCARBAMATE RESIN PREPARATION

The procedure used for preparation of the polydithiocarbamate resin is that of Hackett and Siggia [3] as modified by Bary and Reilly [4].

1. Dissolve 72 g polyethyleneimine*, molecular weight 1800, in 1 L tetrahydrofuran and 28 g polymethylenepolyphenyl isocyanate in 1 L tetrahydrofuran.
2. Pour these two solutions simultaneously into a large flask, allowing the two streams to mix before entering the flask.
3. Let this mixture stand at least 12 hrs with occasional mild agitation, then remove the solvent by filtration.
4. Wash the product twice with methanol and once with deionized water.
5. Add the product to 300 mL carbon disulfide, 100 mL ammonium hydroxide and 500 mL isopropyl alcohol; let stand 72 hrs.
6. Filter to remove the resin from the solvent mixture. Wash the resin three times with methanol and allow it to dry.
7. Grind and sieve the resin, saving the 60/80 mesh size for use.

*Polyethyleneimine stored for one year would not dissolve in the solvent; however, fresh polyethyleneimine readily dissolved.

FORMULA:  ; C_6HCl_5O

M.W.: 266.33

PENTACHLOROPHENOL IN BLOOD

METHOD: 8001
ISSUED: 2/15/84

BIOLOGICAL INDICATOR OF: exposure to pentachlorophenol.

SYNONYMS: PCP; Penta; CAS #87-86-5.

BIOLOGICAL SAMPLING	MEASUREMENT
SPECIMEN: whole blood in 5-mL tubes	TECHNIQUE: GAS CHROMATOGRAPHY, ECD
VOLUME: 5 mL	ANALYTE: pentachloroanisole (PCP methyl ether)
PRESERVATIVE: none	INJECTION VOLUME: 5 µL
SHIPMENT: polyethylene shippers with sample container kept at 10 °C	COLUMN: 1.8 m x 4 mm ID glass, 4% SE-30, 6% OV-210 on 80/100 mesh silanized support
ANTICOAGULANT: EDTA	CARRIER GAS: 5% methane in argon, 60 mL/min
STABILITY: unknown	TEMPERATURES-INJECTOR: 220 °C -COLUMN: 190 °C -MANIFOLD: 250 °C -DETECTOR: 300 °C
CONTROLS: collect at least 3 blood specimens from unexposed individuals per study or one control per 10 samples for studies exceeding 30 samples	CALIBRATION: solutions of pentachloroanisole in hexane
	QUALITY CONTROL: spiked pooled blood
	RANGE: 0.01 to 1 µg PCP/mL blood
	ESTIMATED LOD: 0.001 µg PCP/mL blood
	RECOVERY: 90%
	PRECISION (s_r): 0.02

APPLICABILITY: This procedure measures free PCP. It is useful for monitoring PCP exposures via skin contact, inhalation, and ingestion. Blood PCP exposures are good indicators of acute short-term exposures because blood PCP values reach maximum 4 hrs after exposure [1]. Chronic exposures can best be monitored using Method 8303, Pentachlorophenol in urine.

INTERFERENCES: Chloronaphthalenes, polychlorinated biphenyl and Diuron are also hexane-extractable but are separated from PCP by column chromatography.

OTHER METHODS: This method is based on that of Borsetti [2].

REAGENTS:

1. Hexane, acetone, and benzene* (pesticide grade).
2. 20% benzene in hexane (v/v); 10% benzene in hexane (v/v).
3. Sulfuric acid, 6 M.
4. Sodium bisulfite.
5. Sodium sulfate, anhydrous.
6. Alumina (acid-washed), Brockman Activity I, 80/200 mesh.
7. Pentachloroanisole (available from EPA Analytical Reference Lab).
8. Calibration stock solution equivalent to 100 mg PCP/L. Weigh 0.0105 g pentachloroanisole; dilute to 100 mL with hexane in a volumetric flask. Stable 2 months if stored in refrigerator.
9. Diazomethane* prepared from Diazald kit according to manufacturer's instructions [3].
10. 5% methane in argon.

*See Special Precautions.

EQUIPMENT:

1. Blood-sampling tubes, 5-mL, with 7.5 mg Na_2EDTA anticoagulant (e.g., "lavender-top" tubes).
2. Gas chromatograph with a ^{63}Ni electron capture detector, electronic integrator, and column (page 8001-1).
3. Culture tubes, 16 x 150 mm and 16 x 125 mm, with PTFE-lined screw caps.*
4. Mixer, rotary, variable speed.
5. Centrifuge (refrigerated, optional).
6. Chromatography column, 7 mm ID x 200 mm, with a 50-mL reservoir and Teflon stopcock.*
7. Syringe, 10-µL, glass.
8. Pipets, 10- to 1000-µL.*
9. Flasks, volumetric, 10-, 25-, and 100-mL.*
10. Pipets, Pasteur, disposable.
11. Tubes, centrifuge, graduated, glass-stoppered, 15-mL.*
12. Waterbath, 100 °C.

*Wash with detergent; clean with chromic acid; rinse with distilled water, acetone, and hexane.

SPECIAL PRECAUTIONS: Benzene is a documented human carcinogen and must be handled in compliance with 29 CFR 1910.1005.

Diazomethane and its precursor, n-Methyl-n-nitroso-p-toluene sulfonamide, are potent mutagens. Handle the bulk precursor in a glove box. Generate diazomethane behind and explosion shield in a hood.

SAMPLING:

1. Collect 5-mL whole blood samples by venipuncture in tubes containing 7.5 mg Na_2EDTA anticoagulant, about 4 hrs after suspected exposure.
2. Ship the blood samples in an insulated container with refrigerant to keep the temperature at about 10 °C. Do not freeze.

SAMPLE PREPARATION:

3. Add 2 mL whole blood to a 16 x 150 mm culture tube. Add cautiously and slowly 5 mL 6 M sulfuric acid. Cool to room temperature.
4. Add 6 mL hexane to the culture tubes in a hood; cap and place in a boiling waterbath for 45 min with shaking every 15 min.
5. Cool the culture tubes to room temperature and centrifuge at 2000 to 2500 rpm.
6. Remove the hexane layer into a 16 x 125 mm culture tube.
7. Extract twice more with 2 mL hexane for 2 min. Combine the extracts.
8. Concentrate the combined extracts to approximately 0.6 mL under a gentle stream of nitrogen.
9. Add 10 mL diazomethane reagent to the culture tube in a hood. Let stand in a hood for 1 hr.

10. Concentrate to approximately 0.6 mL under a gentle stream of nitrogen in a hood.
11. Add 4 mL hexane. Evaporate the hexane solution to approximately 0.6 mL.
12. Add 4 g acid-washed alumina to a 7-mm ID x 200 mm chromatography column. Cap with 1.6 g anhydrous sodium sulfate. Rinse the column with 20% benzene in hexane. Let the column air dry and place it in an oven overnight at 130 °C. Cool the column to room temperature before use.
13. Wet the column with 5 mL hexane in a hood.
14. Add the concentrated derivatized extract when the solvent layer reaches the top of the sodium sulfate layer.
15. Rinse the culture tube three times with 0.5 mL hexane. Add the rinsings to the column.
16. Add 3.5 mL hexane to the column. Discard the hexane eluate.
17. Elute pentachloroanisole, the PCP derivative, with 20 mL 10% benzene in hexane.
18. Concentrate the sample to 2.0 mL in a graduated centrifuge tube.

CALIBRATION AND QUALITY CONTROL:

19. Prepare at least 6 working standards in the range 0.01 to 1 µg PCP/mL by dilution of the calibration stock solution with hexane.
20. Prepare a calibration graph (concentration of standard, µg PCP/mL vs. area of analyte peak).
21. Maintain standardization by injecting a working standard after each five sample injections.
22. Run a spiked pooled control blood sample every ten samples, or if less than ten determinations are required, run at least three spiked pooled blood samples per study.
    NOTE: All blood that will be utilized for spiked pooled control blood samples must be analyzed for PCP before use because PCP is ubiquitous.

MEASUREMENT:

23. Set up the gas chromatograph according to manufacturer's instructions and to the conditions on page 8001-1.
24. Inject 5 µL sample extract (from step 18). Measure peak area of analyte.
    NOTE: The retention time for pentachloroanisole is about 4.7 to 5.0 min.

CALCULATIONS:

25. Determine the concentration, C (µg/mL), of PCP in blood by comparison of peak areas of samples with the calibration graph.

GUIDES TO INTERPRETATION:

Blood PCP levels for unexposed populations range between 0.016 to 0.32 µg PCP/mL [4,5,6].

EVALUATION OF METHOD:

The precision for three sets of three samples of spiked whole blood was 2% relative standard deviation at levels of 0.05 to 1 µg PCP/mL whole blood, with 88 to 93% recovery.

REFERENCES:

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[3] Diazald, Cat. No. 02800-0, Aldrich Chem. Co. Inc., Milwaukee, WI.

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[5] Casarett, L.J., Bevenue, A., Yauger, W.L., and Whalen, S.A. Observation on Pentachlorophenol in Human Blood and Urine, Am. Ind. Hyg. Assoc. J., 360-365 (July-August, 1969).

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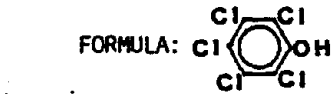
METHOD WRITTEN BY: Anthony W. Smallwood and Karl E. DeBord, NIOSH/DBBS.

FORMULA:  ;C_6HCl_5O

M.W.: 266.33

PENTACHLOROPHENOL IN URINE

METHOD: 8303
ISSUED: 2/15/84

BIOLOGICAL INDICATOR OF: exposure to pentachlorophenol.

SYNONYMS: PCP; Penta; CAS #87-86-5.

BIOLOGICAL SAMPLING	MEASUREMENT
SPECIMEN: urine end of shift, mid to late in work week	TECHNIQUE: GAS CHROMATOGRAPHY, ECD
VOLUME: 100 mL in polyethylene bottle	ANALYTE: pentachloroanisole (PCP methyl ether)
PRESERVATIVE: 2 to 3 drops concentrated HCl added after collection	INJECTION VOLUME: 5 µL
SHIPMENT: ship frozen in dry ice	COLUMN: 1.8 m x 4 mm ID glass, 4% SE-30, 6% OV-210 on 80/100 mesh silanized support
STABILITY: 40 days if kept frozen	CARRIER GAS: 5% methane in argon, 60 mL/min
CONTROLS: collect 3 urine specimens from unexposed workers per study or 1 control urine per 10 samples	TEMPERATURES-INJECTOR: 220 °C -COLUMN: 190 °C -MANIFOLD: 250 °C -DETECTOR: 300 °C
	CALIBRATION: solutions of pentachloroanisole in hexane
	QUALITY CONTROL: spiked urine pools; corrected for creatinine content
	RANGE: 1 to 1000 µg/L
	ESTIMATED LOD: 1 µg/L [4]
	RECOVERY: 0.947
	PRECISION (s_r): 0.03 [4]

APPLICABILITY: This method measures free and conjugated PCP after hydrolysis and is useful when monitoring chronic PCP exposure via skin contact, ingestion or inhalation. Maximum urine levels are found 42 hrs after exposure [1]. Acute exposures are best monitored using Method 8001, Pentachlorophenol in blood [2]. Urine contains about 82% free PCP and 13% PCP glucuronide [1].

INTERFERENCES: Numerous potential interferences that can be extracted from urine include chloronaphthylenes, polychlorinated biphenyls and Diuron; these are eliminated by sample cleanup.

OTHER METHODS: This method combines and replaces P&CAM 230 [3] and P&CAM 358 [4].

REAGENTS

1. Hexane, acetone, and benzene* (pesticide grade).
2. 20% benzene in hexane (v/v).
3. 10% benzene in hexane (v/v).
4. Hydrochloric acid (conc.).
5. Sodium bisulfite.
6. Sodium sulfate.
7. Alumina (acid-washed), Brockman Activity I, 80/200 mesh.
8. Pentachloroanisole (available from EPA Analytical Reference Lab).
9. Calibration stock solution equivalent to 100 mg PCP/L. Weigh 0.0105 g pentachloroanisole; dilute to 100 mL in a volumetric flask with hexane. Stable 2 months if stored in refrigerator.
10. Diazomethane*. Prepared from Diazald kit according to manufacturer's instructions [5].
11. 5% methane in argon.

*See Special Precautions.

EQUIPMENT:

1. Bottles, polyethylene, 125-mL, screw cap.*
2. Gas chromatograph with ^{63}Ni electron capture detector.
3. Culture tubes, 16 x 150 mm and 16 x 125 mm, with with PTFE-lined screw caps.*
4. Mixer, rotary, variable speed.
5. Centrifuge (refrigerated, optional).
6. Chromatography column, 7 mm ID x 200 mm, with a 50-mL reservoir and PTFE stopcock.*
7. Syringes, 10-µL, glass.
8. Pipets, 1000-, 500-, 250-, 100-, 50-, 25- and 10-µL.*
9. Flasks, volumetric, 10- and 100-mL.*
10. Pipets, Pasteur, disposable.
11. Tubes, centrifuge, graduated, glass-stoppered, 15-mL.*
12. Waterbath, 100 °C.

*Wash with detergent; clean with chromic acid; rinse with distilled water, acetone, and hexane.

SPECIAL PRECAUTIONS: Benzene is a documented human carcinogen and must be handled in compliance with 29 CFR 1910.1005.

Diazomethane and its precursor, n-Methyl-n-nitroso-p-toluene sulfonamide are potent mutagens. Handle the bulk precursor in a glove box. Generate diazomethane behind an explosion shield in a hood.

SAMPLING:

1. Collect a spot urine sample of 100 mL in a 125-mL polyethylene bottle.
2. Add two or three drops conc. HCl to the sample as a preservative.
3. Freeze the samples and pack them in an insulated shipper (e.g., styrofoam with dry ice).

SAMPLE PREPARATION:

4. Perform a creatinine determination on an aliquot of the urine (e.g., [11]).
5. Transfer a 4-mL aliquot of each urine sample to a 16 x 150 mm culture tube.
6. Add 1.0 mL conc. HCl and 100 mg sodium bisulfite to each culture tube.
7. Cap and place the culture tubes in a boiling waterbath for 1 hr. Shake gently at 15-min intervals.
8. Cool the culture tubes to room temperature.
9. Add 5 mL benzene to each culture tube. Extract on a rotary mixer at 60 rpm for 1 hr.
10. Centrifuge at 3000 rpm. Transfer benzene layer to a 16 x 125 mm culture tube. Repeat the extraction with an additional 5 mL benzene. Combine extracts.
11. Concentrate the extract to approximately 0.6 mL under a gentle stream of nitrogen.

12. Add 10 mL of diazomethane reagent (use hood). Let stand under hood for 1 hr.
13. Concentrate under a hood to 0.6 mL under a gentle stream of nitrogen.
14. Add 4 mL hexane. Evaporate the solution to approximately 0.6 mL.
15. Add 4 g acid-washed alumina to a 7-mm ID x 200 mm chromatography column. Cap with 1.6 g anhydrous sodium sulfate. Rinse the column with 20% benzene in hexane. Air-dry. Place the column in a 130 °C oven overnight. Cool the column to room temperature before use.
16. Wet the column with 5 mL hexane (use fume hood).
17. Add the concentrated derivatized extract when the solvent layer reaches the top of the sodium sulfate layer.
18. Rinse the culture tube three times with 0.5 mL hexane. Add the rinsings to the column.
19. Add 3.5 mL hexane to the column. Discard the hexane eluate.
20. Elute pentachloroanisole, the PCP derivative, with 20 mL 10% benzene in hexane.
21. Concentrate the sample to 2.0 mL in a graduated centrifuge tube.

CALIBRATION AND QUALITY CONTROL:

22. Prepare at least six working standards in the range 5 to 1000 µg PCP/L by dilution of the calibration stock solution with hexane.
23. Prepare a calibration graph (concentration of standard, µg PCP/L vs. area of analyte peak).
24. Maintain standardization by injecting a working standard after each five sample injections.
25. Run a spiked urine every ten samples or if less than ten determinations are required, run at least three spiked urines per run or study.
    NOTE: Urine used for spikes must be analyzed before use to determine background levels.

MEASUREMENT:

26. Set up the gas chromatograph according to manufacturer's instructions and to conditions on page 8303-1.
27. Inject 5-µL sample extract from step 21. Measure peak area of analyte.
    NOTE: The retention time for pentachloroanisole is about 4.7 to 5.0 min.

CALCULATIONS:

28. Use the analyte peak area from the samples and the calibration graph to determine the PCP concentration in the extract analyzed, C_e (µg PCP/L).
29. Calculate the urine PCP concentration, C (µg PCP/L), by applying the extract concentration factor 2 (4 mL urine yields 2 mL extract):

$$C = 0.5C_e, \text{ µg PCP/L.}$$

30. Express PCP concentration as µg PCP/g creatinine.

GUIDES TO INTERPRETATION:

Urine pentachlorphenol levels for unexposed populations are reported to be between 20 and 40 µg PCP/L [6,7,8]. Symptoms have been reported at 200 µg PCP/L and levels in excess of 20 mg/L are fatal [7,9]. Lauwerys suggests an upper limit of 1 mg/g creatinine [10].

EVALUATION OF METHOD:

The recovery of PCP from spiked urine samples was 93 to 96% for specimens containing 5 to 1000 µg PCP/L urine. The recovery of PCP from frozen urine samples spiked with 100 ng PCP/L urine and stored up to 36 days ranged from 85 to 91%.

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[2] This Manual, Method 8001.

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METHOD WRITTEN BY: Anthony W. Smallwood and Karl E. DeBord, NIOSH/DBBS; and Robert Kurimo, NIOSH/DPSE.

FORMULA: $C_{12}H_{10-x}Cl_x$ (x = 1 to 10)

POLYCHLOROBIPHENYLS IN SERUM

METHOD: 8004

M.W.: 188 to 498

ISSUED: 2/15/84

BIOLOGICAL INDICATOR OF: exposure to PCB.

SYNONYMS: Aroclor; PCB; chlorodiphenyl; CAS #53469-21-9; CAS #11097-69-1.

BIOLOGICAL SAMPLING	MEASUREMENT
SPECIMEN: serum	TECHNIQUE: CAPILLARY COLUMN GAS CHROMATOGRAPHY, ECD
VOLUME: 10 mL	INJECTION VOLUME: 3 µL, Grob type splitless
PRESERVATIVE: none	COLUMN: 15 m x 0.2 mm ID, WCOT SE-54
SHIPMENT: polyethylene shippers @ 10 °C	CARRIER GAS: 5% methane in argon, 1 mL/min
STABILITY: indefinite if serum is kept frozen	TEMPERATURE-INJECTOR: 260 °C -COLUMN: 100 °C for 2 min; 20 °C/min to 260 °C for 4 min -DETECTOR: 350 °C
CONTROLS: collect 3 specimens from unexposed populations per study or 1 per 10 unknowns for studies exceeding 30 specimens	CALIBRATION: hexane solutions of Aroclors 1016, 1221, 1232, 1242, 1248, 1254 and 1260
BULK: submit a bulk sample of material to which workers were exposed	QUALITY CONTROL: pooled or spiked serum
	RANGE: 0.005 to 1.0 µg/mL
	ESTIMATED LOD: 0.001 µg/mL
	RECOVERY: greater than 80%
	PRECISION (s_r): 0.16

APPLICABILITY: Since PCBs are rapidly absorbed from the lung, GI tract, and skin, this procedure is useful for estimating acute and chronic exposures to PCB, assuming (a) no metabolism of PCB, (b) all isomers of PCB are extracted with equal efficiency, and (c) similar ECD response for all PCBs. PCBs have a high degree of biological and chemical stability. They accumulate in adipose tissue and may present a serious latent health threat. Metabolism involves hydroxylation and conjugation with glucose and sulfates.

INTERFERENCES: Chlorinated hydrocarbons, phthalate based plasticizers, dibenzofurans, and chlorinated naphthalenes interfere.

OTHER METHODS: This method replaces P&CAM 329 [1]. Other methods include a screening method for Aroclor 1254 in whole blood [2].

REAGENTS:

1. Methanol, hexane, ethyl ether, and acetone (pesticide grade).
2. Potassium hydroxide, KOH.
3. Calibration stock solutions, 0.1 mg/mL.* Dissolve 10 mg of the bulk sample or other suitable standard, e.g., Aroclor 1016, 1221, 1232, 1242, 1248, 1254, and 1260 in 100 mL n-hexane (standards available from EPA).
4. Silica gel, activity grade I.
   a. Heat to 130 °C for 24 hrs.
   b. Cool and add 3 g water per 100 g silica gel. Mix for 2 hrs in a sealed container.
5. Sodium sulfate (anhydrous).
6. 1,1-Dichloro-2,2-bis (p-chlorophenyl)ethylene (DDE) solution, 50 ng/mL, in hexane.
7. Methanolic KOH, 2% (w/v). Dissolve 2 g KOH in methanol to make 100 mL solution.
8. Methanol-water, 1:1 (v/v).
9. Hexane-ethyl ether, 1:1 (v/v).
10. Nitrogen, compressed, filtered.

*See Special Precautions.

EQUIPMENT:

1. Gas-liquid chromatograph equipped with an electron capture detector.
2. Syringes, glass, 30-mL.*
3. Culture tubes, 16- x 150-mm, organic-free, with PTFE-lined screw caps.*
4. Rotary mixer, variable speed.
5. Centrifuge.
6. Kuderna-Danish concentrator tubes, 25-mL.*
7. Micro-Synder columns.*
8. Tube heater.
9. Chromatography column, 7 mm ID x 200 mm, with 50-mL reservoir and PTFE stopcock.*
   a. Put a small plug of glass wool in the bottom of the column.
   b. Pour a suspension of 3 g silica gel in 50-mL hexane into the column.
   c. Let the suspension settle and add 5 to 7 g sodium sulfate.
10. Syringes, 10-µL, glass.
11. Graduated cylinder, 25-mL.*
12. Pipet, Pasteur.

*Clean all glassware, including that used in sampling as follows: Wash in detergent. Rinse with tap water. Soak in chromic acid. Rinse with, in order, tap water, distilled water, acetone and hexane.

SPECIAL PRECAUTIONS: PCBs have potential carcinogenicity in humans. They are microsomal enzyme inducers and liver toxins; therefore, use extreme caution when handling these substances [3].

SAMPLING:

1. Collect 20 to 25 mL whole blood samples by venipuncture via 30-mL glass syringe.
2. After the blood has clotted, centrifuge for 10 min at 2000 rpm. Transfer the serum to a 16 x 150 mm culture tube with a PTFE-lined screw cap.
3. Ship the serum in an insulated container with bagged refrigerant to keep the samples at 4 °C.
4. Freeze the samples upon arrival at the laboratory.

SAMPLE PREPARATION:

5. Pipet 5 mL serum into a clean culture tube containing 4 mL methanol.
6. Cap the tube and mix 4 min on a rotary mixer.
7. Add 5 mL hexane-ethyl ether (1:1, v/v).
8. Mix on a rotary mixer for 15 min.
9. Centrifuge at 2000 rpm for 5 min.
10. Transfer the upper solvent layer by pipet into a 25 mL Kuderna-Danish concentrator tube.
11. Repeat steps 7 through 10 twice, combining the extracts in the concentrator tube.
12. Concentrate the extract to 0.5 mL under a gentle stream of dry organic-free nitrogen.

13. Add 2 mL methanolic KOH to the concentrator tube. Add a piece of hollow glass (end of a Pasteur pipet) to prevent bumping.
14. Attach a micro-Synder column and bring the contents to a gentle boil with a tube heater and reduce the volume to 0.3 mL.
    NOTE: If a precipitate forms, add a few drops of methanolic KOH solution and warm gently with a tube heater until it dissolves.
15. Cool the solution slightly and add 2 mL 1:1 methanol:water.
16. Add 2 mL n-hexane when the solution reaches room temperature.
17. Stopper and shake the tube vigorously.
18. Rinse the prepared chromatography column (EQUIPMENT, 9.) with 20 mL hexane. As the hexane settles into the sodium sulfate bed, add the sample.
19. Place a 25-mL graduated cylinder below the chromatographic column.
20. Rinse the concentrator tube and the micro-Synder column with 1 mL hexane.
21. As the saponified extract enters the sodium sulfate layer, add the concentrator tube and micro-Synder column rinses to the chromatographic column.
22. As the rinses settle in the sodium sulfate layer, add 25 mL hexane.
23. Collect 25 mL eluate from the column in the graduated cylinder.
24. Rinse the walls of the graduated cylinder with 2 mL hexane.
25. Concentrate to 1 mL under a gentle stream of nitrogen.

CALIBRATION AND QUALITY CONTROL:

26. Analyze the bulk sample for PCB content [4].
27. Calibrate daily with at least five working standards over the range 0.005 to 1 µg PCB/mL.
    a. Add known amounts of calibration stock solution to n-hexane in 10-mL volumetric flasks and dilute to the mark with n-hexane.
    b. Analyze the working standards together with samples and blanks (steps 29 and 30).
    c. Prepare calibration graph (concentration of each PCB standard vs. the sum of PCB peak areas).
28. Analyze at least three pooled or spiked serum samples.

MEASUREMENT:

29. Set gas chromatograph according to manufacturer's instructions and conditions on page 8004-1. Inject 2 µL sample together with 1 µL DDE solution.
30. Measure the PCB peak areas. Calculate the retention time of the analyte peaks relative to that of DDE.

CALCULATIONS:

31. Compare sample retention times (relative to DDE) with those of the working standards and bulk sample to ascertain the valid PCB peaks.
32. Read the concentration of PCB in the hexane solution (µg/µL) from the calibration graph.
33. Calculate the serum PCB concentration, C (µg PCB/mL), by dividing the PCB concentration found in the extract, C_e, by 5 (5 mL serum yields 1 mL extract):

$$C = 1/5\ C_e\ (\mu g\ PCB/mL).$$

GUIDES FOR INTERPRETATION:

PCBs are present in the biosphere. Baselt [5] indicates a level 2 to 4 µg/L of plasma is indicative of significant exposure. Finklea [6] reported 57% of individuals tested had levels below 5 µg/L. Most control populations have PCB levels below 20 µg/L serum. What levels

present a health hazard is not documented; however, a 0.2 µg/L as an upper limit has been suggested [7]. If a serious exposure is suspected, then the serum PCB levels should be augmented by liver battery and triglyceride tests plus a complete medical evaluation to ascertain the employee health risk.

EVALUATION OF METHOD:
Eighty-nine analyses of four spiked human serum for the Aroclors 1242 and 1254 with a concentration range of 0.025 to 0.400 µg/L indicated recoveries greater than 80% with precision, s_r, of 0.16 [8].

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METHOD WRITTEN BY: Anthony W. Smallwood, Karl E. DeBord, and Larry K. Lowry, Ph.D., NIOSH/DBBS.

BULK SAMPLES

9000-1

FORMULA: $Mg_3Si_2O_5(OH)_4$

M.W.: ca. 283

CHRYSOTILE ASBESTOS

METHOD: 9000
ISSUED: 2/15/84

EPA Standard (Bulk): 1% by weight

PROPERTIES: solid, fibrous mineral; conversion to Forsterite at 580 °C; attacked by acids; loses water above 300 °C

SYNONYMS: Chrysotile; CAS #12001-29-5.

SAMPLING

BULK SAMPLE: 1 to 10 grams

SHIPMENT: seal securely to prevent escape of asbestos

SAMPLE STABILITY: indefinitely

BLANKS: none required

ACCURACY

RANGE STUDIED: 1 to 100% in talc [3]

BIAS: negligible if standards and samples are matched in particle size [3]

OVERALL PRECISION (s_r): unknown; depends on matrix and concentration

MEASUREMENT

TECHNIQUE: X-RAY POWDER DIFFRACTION

ANALYTE: chrysotile

PREPARATION: grind under liquid N_2; wet-sieve through 10-µm sieve

DEPOSIT: 5 mg dust on 0.45-µm Ag membrane filter

XRD: Cu target X-ray tube
Optimize for intensity; 1° slit
Integrated intensity with background subtraction

CALIBRATION: suspensions of asbestos in 2-propanol

RANGE: 1 to 100% (w/w) asbestos

ESTIMATED LOD: 0.2% asbestos in talc and calcite; 0.4% in heavy X-ray absorbers such as Fe_2O_3

PRECISION (s_r): 0.07 (5 to 100%); 0.10 (at 3%); 0.125 (at 1%)

APPLICABILITY: Analysis of percent chrysotile asbestos in bulk samples.

INTERFERENCES: Antigorite (massive serpentine), Chlorite, Kaolinite, Bementite, and Brushite. X-ray fluorescence and absorption is a problem with some elements; fluorescence can be circumvented with a diffracted beam monochromator, and absorption is corrected for in this method.

OTHER METHODS: This is P&CAM 309 [2] applied to bulk samples only, since the sensitivity is not adequate for personal air samples. The EPA Test Method for the determination of asbestos in bulk insulation samples is similar to this one [4]. Method 7400 is an optical counting procedure for airborne fibers in personal samples.

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REAGENTS:

1. Chrysotile*, available from:
   Analytical Reference Minerals,
   Measurements Research Branch,
   DPSE, NIOSH, 4676 Columbia Parkway,
   Cincinnati, OH 45226; or
   UICC Asbestos Reference Sample Set,
   UICC MRC Pneumoconiosis Unit
   Llandough Hospital, Penarth,
   Glamorgan, CF6 1XW, UK.2.
2. 2-Propanol.*
3. Desiccant.
4. Glue or tape for securing Ag filters to XRD holders.

*See Special Precautions.

EQUIPMENT:

1. Vials, plastic (for bulk sample).
2. Freezer mill, liquid N_2-cooled, (Spex Model 6700 or equivalent), grinding vials (Spex 6701), extractor (Spex 6704).
3. Ultrasonic bath.
4. Sieve, 10-µm, for wet-sieving.
5. Filters, polycarbonate, 1.0-µm, 37-mm (Nuclepore or equivalent).
6. Filtration apparatus and side-arm vacuum flask with 25- and 37-mm filter holders.
7. Oven, drying, 110 °C.
8. Analytical balance, readable to 0.01 mg.
9. Beaker, Griffin, 50-mL, with watchglass cover.
10. Filters, silver membrane, 25-mm diameter, 0.45-µm pore size (Selas Flotronics, Dresher, PA 19006, or equivalent).
11. Desiccator.
12. Bottles, glass, 1-L, with ground glass stoppers.
13. Wash bottle, polyethylene.
14. Magnetic stirrer.
15. X-ray powder diffractometer with copper target X-ray tube and scintillation detector.
16. Reference specimen (mica, Arkansas stone or other stable standard) for data normalization.
17. Volumetric pipettes and flasks.

SPECIAL PRECAUTIONS: Asbestos, a human carcinogen, should be handled in a hood [1].

2-Propanol is flammable.

SAMPLING:

1. Place several grams of the dust to be analyzed in a plastic vial, seal the vial securely and ship in a padded carton.

SAMPLE PREPARATION:

2. Place ca. 0.5 g of sample dust in a grinding vial and grind in a liquid nitrogen-cooled mill for 2 to 10 min.
3. Wet sieve the ground dust using a 10-µm sieve and 2-propanol. Place the dust on the sieve and place the sieve directly in an ultrasonic bath or in a wide dish in the bath. Use enough 2-propanol to cover the dust (put water in the bath if a dish is used to contain the 2-propanol). Apply ultrasonic power to sieve the dust.
   NOTE: It may take some time to obtain several mg of dust. Heating of the 2-propanol is likely and cooling periods may be required.
4. Recover the sieved sample dust from the 2-propanol by filtering the suspension through a non-fibrous filter (polycarbonate) or by driving off the 2-propanol on a hot plate. Dry the sieved sample in 110 °C oven for 4 hrs or more.

5. Weigh out ca. 5 mg of the sieved material onto a small square of tared weighing paper. Record the actual weight, W, to the nearest 0.01 mg. Transfer the dust to a 50-mL beaker, washing the weighing paper with several mL of 2-propanol. Add 10 to 15 mL 2-propanol to the beaker.
6. Cover the beaker with a watchglass. Agitate in an ultrasonic bath at least 3 min until all agglomerated particles are dispersed. Wash the underside of the watchglass with 2-propanol, collecting the washings in the beaker.
7. Place a silver filter in the filtration apparatus. Attach the funnel securely over the entire filter circumference. With no vacuum, pour 2 to 3 mL 2-propanol onto the filter. Pour the sample suspension from the beaker into the funnel and apply vacuum. During filtration, rinse the beaker several times and add rinsings to the funnel.
   NOTE: Control the filtration rate to keep the liquid level in the funnel near the top during rinsing. Do not wash the walls or add 2-propanol to the funnel when the liquid level is lower than 4 cm above the filter. Leave the vacuum on after filtration for sufficient time to produce a dry filter.
8. Remove the filter with forceps and attach it to the sample holder for XRD analysis.

CALIBRATION AND QUALITY CONTROL

9. Prepare and analyze working standard filters:
   a. Prepare two suspensions of chrysotile asbestos in 2-propanol by weighing 10 and 100 mg of the dry powder to the nearest 0.01 mg. Quantitatively transfer each to a 1-L glass-stoppered bottle using 1.00 L 2-propanol.
      NOTE: Depending on the particle size of the standard, it may need to be ground and wet-sieved (step 3). Dry the standards in a 110 °C oven for 4 hrs or more. Store in a dessicator.
   b. Suspend the powder in the 2-propanol with an ultrasonic probe or bath for 20 min. Immediately move the flask to a magnetic stirrer with thermally-insulated top and add a stirring bar to the suspension. Cool the solution to room temperature before withdrawing aliquots.
   c. Mount a filter on the filtration apparatus. Place several mL 2-propanol on the filter surface. Turn off the stirrer and shake vigorously by hand. Within a few seconds of setting the bottle down, remove the lid and withdraw an aliquot from the center of the 10-or 100-mg/L suspension. Do not adjust the volume in the pipet by expelling part of the suspension. If more than the desired aliquot is withdrawn, return all of the suspension to the bottle, rinse and dry the pipet, and take a new aliquot. Transfer the aliquot from the pipet to the filter. Keep the tip of the pipet near the surface but not submerged in the delivered suspension.
   d. Rinse the pipet with several mL 2-propanol, draining the rinse into the funnel. Repeat the rinse several more times. Prepare working standard filters, in triplicate, by this technique, at e.g., 0, 20, 30, 50 100, 200 and 500 µg.
   e. Apply vacuum and rapidly filter the suspension. Leave vacuum on until filter is dry. Do not wash down the sides of the funnel after the deposit is in place since this will rearrange the material on the filter. Transfer the filter to the sample holder.
   f. Analyze by XRD (step 12). The XRD intensities (12.d.) are designated I_x^o and are then normalized (12.e.) to obtain $\hat{I}_x^o$. The intensities for standards greater than 200 µg should be corrected for matrix absorption (12.f. and 13).
   g. Prepare a calibration graph by plotting $\hat{I}_x^o$, as a function of µg of each standard.
      NOTE: Poor repeatability (greater than 10% above 0.04 mg chrysotile) at any given level indicates that new standards should be made. The data should lie along a straight line. It is preferable to use a weighted least squares with $1/\sigma^2$ weighting, where σ^2 is the variance of the data at a given loading.

h. Determine the slope, m, of the calibration curve in counts/µg. The intercept on the abscissa should be within ± 5 µg of zero.
NOTE: A large intercept indicates an error in determining the background, i.e., an incorrect baseline has been calculated or interference by another phase.

10. Select six silver membrane filters as media blanks (to test for sample self-absorption) randomly from the same box of filters to be used for depositing the samples. Mount each of the media blanks on the filtration apparatus and apply vacuum to draw 5 to 10 mL of 2-propanol through the filter. Remove, let dry and mount on sample holders. Determine the net normalized count for the silver peak, $\hat{I}^{0}_{Ag}$, for each media blank (step 12). Obtain an average value for the six media blanks.

MEASUREMENT:

11. Obtain a qualitative X-ray diffraction scan (e.g., 10 to 80 degrees 2-theta) of the sample to determine the presence of chrysotile and interferences. The expected diffraction peaks are as follows:

	Peak (2-Theta Degrees)	
Mineral	Primary	Secondary
Chrysotile	12.08	24.38
Silver	38.12	44.28

12. Mount the filter (sample, standard or blank) in the XRD instrument and:
a. Determine the net intensity, I_r, of the reference specimen before each filter is scanned. Select a convenient normalization scale factor, N, which is approximately equivalent to the net count for the reference specimen peak, and use this value of N for all analyses.
b. Measure the diffraction peak area of a chrysotile peak that is free of interference. Scan times should be long, e.g., 15 min.
c. Measure the background on each side of the peak for one-half the time used for peak scanning. The sum of these two counts is the average background. Determine the position of the background for each sample.
d. Calculate the net intensity, I_X (the difference between the peak integrated count and the total background count).
e. Calculate and record the normalized intensity, $\hat{I}_X$, for the sample peak on each sample and standard:

$$\hat{I}_X = \frac{I_X}{I_r} \cdot N.$$

NOTE: Normalizing to the reference specimen intensity compensates for long-term drift in X-ray tube intensity. If intensity measurements are stable, the reference specimen may be run less frequently; net intensities should be normalized to the most recently measured reference intensity.

f. Determine the net count, I_{Ag}, of an interference-free silver peak on the sample filter following the same procedure. Use a short scan time for the silver peak (e.g., 5% of scan time for analyte peaks) throughout the method.

CALCULATIONS:

13. Calculate the percentage of chrysotile in the bulk dust sample:

$$C = \frac{(\hat{I}_X \cdot f(T) - b)}{m \times W}, \%$$

where:

$\hat{I}_X$ = normalized intensity for sample peak

b = intercept of calibration graph ($\hat{I}^0_X$ vs. W)

m = slope of calibration graph (counts/µg)

$f(T) = \frac{-R \ln T}{1 - T^R}$ = absorption correction factor (Table 1)

$R = \sin(\Theta_{Ag})/\sin(\Theta_X)$

$T = \hat{I}_{Ag}/(\text{average } \hat{I}^0_{Ag})$ = transmittance of sample

$\hat{I}_{Ag}$ = normalized silver peak intensity from sample

average $\hat{I}^0_{Ag}$ = normalized silver peak intensity from media blanks (average of six values)

W = mass of deposited sample in µg.

NOTE: For a more detailed discussion of the absorption correction procedure, see references [5] to [8].

EVALUATION OF METHOD:

This method is based on the work of B.A. Lange in developing P&CAM 309 [2,3]. Samples in the range of 1 to 100% chrysotile in talc were studied to establish the feasibility of an XRD method for airborne asbestos. Analytical precision was as follows:

% Chrysotile in Talc	S_r (%)
100	6.9
10	4.7
7	9.8
5	8.2
3	10.1
1	12.5

This work also showed that bias of results after absorption corrections are made is essentially negligible.

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[4] EPA Research and Development Report, Test Methods: Interim Method for the Determination of Asbestos in Bulk Insulation Samples, EPA-600/M4-82-020 (1982).

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[8] Dollberg, D. D., M. T. Abell, and B. A. Lange. Occupational Health Analytical Chemistry: Quantitation Using X-Ray Powder Diffraction, ACS Symposium Series, No. 120, 43 (1980).

METHOD REVISED BY: M. T. Abell, NIOSH/DPSE.

Table 1. Absorption correction factor as a function of transmittance for some chrysotile-silver peak combinations.

Transmittance T	Chrysotile Silver	f(T) 12.08 / 38.12	f(T) 24.38 / 38.12	Transmittance T	f(T) 12.08 / 38.12	f(T) 24.38 / 38.12
1.00		1.0000	1.0000	0.69	1.6839	1.3142
0.99		1.0157	1.0078	0.68	1.7151	1.3277
0.98		1.0317	1.0157	0.67	1.7470	1.3414
0.97		1.0480	1.0237	0.66	1.7797	1.3555
0.96		1.0647	1.0319	0.65	1.8132	1.3698
0.95		1.0817	1.0402	0.64	1.8475	1.3845
0.94		1.0991	1.0486	0.63	1.8827	1.3995
0.93		1.1168	1.0572	0.62	1.9188	1.4148
0.92		1.1350	1.0659	0.61	1.9558	1.4305
0.91		1.1535	1.0747	0.60	1.9938	1.4465
0.90		1.1724	1.0837	0.59	2.0328	1.4629
0.89		1.1917	1.0928	0.58	2.0728	1.4797
0.88		1.2114	1.1021	0.57	2.1139	1.4969
0.87		1.2316	1.1115	0.56	2.1560	1.5145
0.86		1.2522	1.1212	0.55	2.1993	1.5325
0.85		1.2733	1.1309	0.54	2.2438	1.5510
0.84		1.2948	1.1409	0.53	2.2895	1.5700
0.83		1.3168	1.1510	0.52	2.3365	1.5895
0.82		1.3394	1.1613	0.51	2.3848	1.6095
0.81		1.3624	1.1718	0.50	2.4344	1.6300
0.80		1.3859	1.1825	0.49	2.4855	1.6510
0.79		1.4100	1.1933	0.48	2.5380	1.6727
0.78		1.4346	1.2044	0.47	2.5921	1.6950
0.77		1.4598	1.2157	0.46	2.6478	1.7179
0.76		1.4856	1.2272	0.45	2.7051	1.7414
0.75		1.5120	1.2389	0.44	2.7642	1.7657
0.74		1.5390	1.2508	0.43	2.8251	1.7907
0.73		1.5666	1.2630	0.42	2.8879	1.8165
0.72		1.5949	1.2754	0.41	2.9526	1.8431
0.71		1.6239	1.2881	0.40	3.0195	1.8705
0.70		1.6536	1.3010			

GLOSSARY

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APPENDIX A. Unit Equivalents

VOLUME

cm^3	liters	m^3	in^3	ft^3	oz (fl, U.S.)
1	0.001	0.000001	0.061024	0.000035315	0.033814
1000	1	0.001	61.024	0.035315	33.814
1000000	1000	1	61024.	35.315	33814.
16.387	0.016387	0.000016387	1	0.0005787	0.55411
28317	28.317	0.028317	1728.	1	957.51
29.574	0.029574	0.000029574	1.8047	0.0010444	1

PRESSURE

atm	mm Hg, 0 °C	in. water, 20 °C	lb/in^2	kg/cm^2	kPa
1	760.	407.51	14.696	1.0333	101.33
0.0013158	1	0.53620	0.019337	0.0013595	0.13332
0.0024539	1.8650	1	0.036062	0.0025354	0.24864
0.068046	51.715	27.730	1	0.070307	6.8947
0.96784	735.56	394.41	1.4223	1	98.066
0.0098692	7.5006	4.0219	0.14504	0.010197	1

CONCENTRATION IN AIR

Gas or Vapor

parts per million	% by volume	mg/m^3
1	0.0001	$M.W./V_m$
10000	1	$M.W. \cdot 10^4/V_m$
$V_m/M.W.$	$V_m/M.W. \cdot 10^4$	1

Aerosol

mg/m^3	particles per cm^3	MPPCF
1	S/1000	S/35310
1000/S	1	0.02832
35310/S	35.31	1

where V_m, the volume of 1 mole of gas, is:

V_m (L) = 62.36 (t, °C + 273.15)/(P, mm Hg)

V_m as a function of t and P

t, °C	p, mm Hg: 640	680	720	760
40	30.51	28.72	27.12	25.70
30	29.54	27.80	26.26	24.87
25	29.05	27.34	25.82	24.46
20	28.56	26.88	25.39	24.05
10	27.59	25.97	24.52	23.23
0	26.62	25.05	23.66	22.41

where S, specific mass in particles/µg, is:

$S = 1/[4\pi/3)(D_S/2)^3 \, d \cdot 10^6]$

where: D_S = Stokes diam., µm
d = particle density, g/cm^3

EXAMPLES (assumes monodisperse aerosol):

Aerosol	D_S, µm	d, g/cm^3	S, p/µg
Steel	10	7.5	250
Quartz	10	2.65	720
Fe_2O_3	5	5.2	2900
Quartz	5	2.65	5800
Quartz	2	2.65	$9 \cdot 10^4$
PbO fume	1	9.5	$2 \cdot 10^5$
PbO fume	0.2	9.5	$2.5 \cdot 10^7$

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Appendix B. Air Concentration Calculations for Comparison to OSHA Standards

OSHA Permissible Exposure Limits (PEL) are set on the basis of mass of toxic substance per unit volume of air at ambient conditions. Therefore, the OSHA PEL in mg/m^3 is absolutely fixed and not subject to corrections for temperature and pressure. This constraint implies that volume concentration of gases in parts per million (ppm) must be with reference to some defined temperature and pressure; these are NTP (25 °C and 760 mm Hg) in the OSHA PEL limit.

The following formulae, therefore, must be used in calculations comparing analytical results to OSHA PEL. Each of the methods in this Manual uses a similar calculation.

Physical Form of Substance Sampled	Unit of Air Concentration	Formula for Direct Comparison With OSHA PEL Table
Gas	ppm	$C_v = \frac{m \cdot 10^3}{V} \cdot \frac{24.46}{M.W.}$
Gas	mg/m^3	$C = \frac{m \cdot 10^3}{V}$
Aerosol	mg/m^3	$C = \frac{m \cdot 10^3}{V}$

where:
- m = actual mass of substance, in mg, found on the sampling device
- V = air volume, L, taken at the sampling site, ambient temperature and pressure
- 24.46 = the volume (L) of 1 mole of gas at 25 °C and 760 mm Hg
- C_v = air concentration, ppm by volume, at 25 °C and 760 mm Hg
- C = air concentration, mg/m^3
- M.W. = molecular weight, grams/mole

Example: A personal sampling pump with a rotameter is calibrated at 25 °C and 630 mm Hg, and then used to sample air at 20 °C and 660 mm Hg for 60 min at a rotameter reading of 1.00 L/min. The analytical lab reports 0.182 mg of allyl chloride (M.W.=76.5) in the sample. What is the air concentration relative to the OSHA PEL?

Solution: 1. The rotameter calibration correction gives the corrected air volume at the sampling site (see p. 23 for the formula):

$$V = 60 \text{ min} \times 1 \frac{L}{\text{min}} \times \left[\frac{630}{660} \times \frac{293.15}{298.15}\right]^{0.5} = 58.1 \text{ L @ 20 °C and 660 mm Hg}$$

2. Concentration of allyl chloride, for comparison with the OSHA PEL, is:

$$C_v = \frac{0.182 \times 1000}{58.1} \times \frac{24.46}{76.5} = 1.00 \text{ ppm}$$

or

$$C = \frac{0.182 \times 1000}{58.1} = 3.13 \text{ mg/m}^3$$

These values indicate that the concentration of allyl chloride is at the OSHA PEL.

IV. GLOSSARY OF ABBREVIATIONS, DEFINITIONS, AND SYMBOLS

AAS	Atomic absorption spectrophotometry.
Acceptable range (biological)	The range of values of a biological monitoring analyte that would be expected in workers with exposure to the environmental chemical in the workplace at or below Federal Standard or TLV-recommended levels. These ranges are often method-specific.
Accuracy	The degree of agreement between a measured value and the accepted reference value. For an individual measurement, it includes the combination of precision and bias (see Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare Publ. (NIOSH) 77-185 and NIOSH Research Report, Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, USDHHS Publ. (NIOSH) 80-133).
ACGIH	American Conference of Governmental Industrial Hygienists, 6500 Glenway Avenue, Building D-5, Cincinnati, OH 45211.
Ashing	The decomposition, prior to analysis, of organic matrix constituents of the sample and sampler. The most common ashing techniques are solvent, acid, or alkali dissolution; alkaline fusion; and oxidation using either low-temperature oxygen plasma or muffle furnace.
ASV	Anodic stripping voltammetry.
B	Media blank reading for a single-section sampler (e.g., membrane filter).
B_b	Media blank reading for back section of a sampler.
B_f	Media blank reading for front section of a sampler.
Bias	Difference between the average measured mass or concentration and reference mass or concentration expressed as a fraction of reference mass or concentration.
Biological monitoring	The measurements of the absorption of an environmental chemical in the worker by analysis of a biological specimen for the chemical agent, its metabolites or some specific effect on the worker.
BP	Boiling point, °C.
Breakthrough	Elution of substance being sampled from the exit end of a sorbent bed during the process of sampling air.
C	Concentration of gaseous, liquid, or solid substance in air, mg/m^3; also acceptable ceiling concentration (for a specified maximum time of exposure) when applied to personal permissible exposure limits.

Calibration graph	Plot of analytical response vs. known mass or concentration of analyte.
CAS #	Chemical Abstracts Service Registry Number.
CE	Collection efficiency, expressed as a decimal fraction.
49 CFR 171-177	Title 49 (Transportation), Code of Federal Regulations. U. S. regulations governing shipment of hazardous materials.
conc.	Concentrated.
Control (biological)	A value or group of values of a biological monitoring parameter collected from workers with little or no occupational exposure to the specific chemical.
C_v	Concentration of gaseous substance in air, parts per million (V/V). In this manual, C_v is referred to NTP such that $C_v = C \times 24.46/M.W.$
CV	See s_r.
d	Density, g/cm^3.
DE	Desorption efficiency; fraction of known quantity of analyte recovered from spiked solid sorbent media blank. DE may be a function of loading, and should be determined by the chemist for each lot of solid sorbent used for sampling, in the concentration range of interest. Plot (mass recovered - average media blank)/mass added vs. (mass recovered - average media blank).
Detection limit	See LOD.
DNE	Do not exceed.
D_s	Stokes diameter.
ECD	Electron capture detector.
EPA	U.S. Environmental Protection Agency.
est	Estimated.
f	Fibers.
FID	Hydrogen-air flame ionization detector.
Field blank	A sampler handled exactly the same as the field samples, except no air is drawn through it. Used to estimate contamination in preparation for sampling, shipment and storage prior to measurement, but <u>not</u> actually subtracted from sample readings (see media blank).
FTIR	Fourier transform infrared spectroscopy.

GC	Gas chromatography.
Hemolysis	Rupture of red blood cells due to improper collection and handling of whole blood.
HPLC	High performance liquid chromatography.
IC	Ion-exchange chromatography; ion chromatography.
ICP-AES	Inductively coupled plasma - atomic emission spectrometry.
Interference equivalent	Mass or concentration of interfering substance which gives the same measurement reading as unit mass or concentration of substance being measured.
IR	Infrared.
LC	Liquid chromatography.
LOD	Limit of detection (detection limit); amount of analyte which can be distinguished from background. A good estimate for most unbiased industrial hygiene analyses (in which media blank levels are typically very small) is three times the standard error (s_e) of the calibration graph.
LOQ	Limit of quantitation; mass of analyte equal to 10 times the standard error (s_e) of the calibration graph; approximately the mass of analyte for which relative standard deviation, s_r, equals 0.10.
LTA	Low temperature (oxygen plasma) ashing.
MCEF	Mixed cellulose ester filter.
Measurement range	Range of substance, in mass per sample, from the LOQ (or from 10 times the LOD, if LOQ is not known) to an upper limit characteristic of the analytical method, e.g., the limit of linearity or the mass at which precision of the method starts to become worse than $s_r = 0.1$.
Media blank	An unexposed sampler, not taken to the field or shipped, used for background correction of sample readings or for recovery studies.
Metabolite	A substance produced directly by a biotransformation of a chemical. For example, phenol in urine is a metabolite of benzene and is representative of benzene absorption in the worker.
MP	Melting point, °C.
mppcf	Million particles per cubic foot.
MS	Mass spectrometry.
M.W.	Molecular weight.

NIOSH	National Institute for Occupational Safety and Health, Centers for Disease Control, U. S. Public Health Service, U. S. Department of Health and Human Services.
Normal range (biological)	The range of values of a biological monitoring analyte that would be expected in workers without exposure to the environmental chemical in the workplace. Normal ranges are often method-specific.
NTIS	National Technical Information Service, Springfield, VA 22161.
NTP	Normal temperature and pressure, 25 °C (298 K) and 760 mm Hg (101.33 kPa), at which the molar volume of an ideal gas is 24.46 L.
OSHA	Occupational Safety and Health Administration, U. S. Department of Labor.
P	Peak (maximum permissible instantaneous) concentration; also pressure.
PAH	Polynuclear aromatic hydrocarbons; PNA; PNAH.
P_c	Pressure, kPa, at which sampling pump was calibrated.
PCM	Phase contrast microscopy.
PEL	OSHA permissible exposure limit, expressed as an airborne concentration.
PID	Photoionization detector.
Plasma, blood	The clear supernatant from whole blood collected with anticoagulants. Blood is collected, mixed with the anticoagulant and centrifuged to separate the plasma from red blood cells. Plasma contains all clotting factors.
PLM	Polarized light microscopy.
PNA	Polynuclear aromatic hydrocarbons; PAH; PNAH.
Pool (biological)	A combination of biological specimens (i.e., urine or serum) from many workers that is used to prepare small aliquots to be run with each batch of analyses. The analyte must be stable in the biological matrix and under the storage conditions used. Aliquots of these pools are analyzed with each batch of samples and the data are used to develop quality control charts.
Precision	The reproducibility of individual measurements of mass or concentration, expressed as standard deviation or relative standard deviation, s_r (q.v.). See Accuracy.
Proficiency testing	Any interlaboratory testing program where stable specimens are sent to participating laboratories for analysis. Results are tabulated by the testing program operator with the purpose of improving laboratory performance.

P_s	Pressure, kPa, at which air sample was taken.
PTFE	Polytetrafluoroethylene; polyperfluoroethylene; tetrafluoroethene homopolymer; Teflon.
PVC	Polyvinyl chloride.
Q	Sampling flow rate, L/min.
Reagent blank	Reagent(s), without analyte added, which are analyzed to determine their contribution to the total blank reading.
Recovery, R	Fraction recovered (see DE); previously associated with Analytical Method Recovery (AMR), a term which is no longer used.
Relative standard deviation	See s_r and Precision.
Respirable dust	Dust deposited in the non-ciliated portions of the lungs. Percent deposition is a function of the particle's aerodynamic diameter. Different definitions for the deposition of respirable dust have been given by the ACGIH, the British Medical Research Council and other groups. Respirable dust is measured by a sampler whose collection efficiency is equivalent to one of these definitions [see International Standards Organization, TC146, "Size Definitions for Particle Sampling," Amer. Ind. Hyg. Assoc. J. 42(5), A64-A68 (1981)].
R_f	In thin-layer chromatography, the ratio of distance travelled by the analyte from point of application to that of the solvent front.
RF	Radio frequency.
Rotameter calibration correction	See V, and Appendix B (page A-2) for an example.
RTECS	Registry of Toxic Effects of Chemical Substances (NIOSH).
Ruggedness test	Partial or complete analysis of variance using experiments in which operational parameters of a sampling and measurement method are varied within a small range to determine their effect on overall variance (see Youden, W. J. and E. H. Steiner, Statistical Manual of the AOAC, Association of Official Analytical Chemists, Arlington, VA, 1975).
s	Estimate of the standard deviation, .
S	Specific mass, particles/µg.
s_b	Estimate of the standard deviation of media blank, .
Screening test (biological)	An easily performed method, often relatively non-specific, to assess worker exposure to a class of compounds by use of biological monitoring.

SEM	Scanning electron microscopy.
Sensitivity	Change in measurement signal per unit change in analyte mass (e.g., slope of calibration graph).
Serum	The clear supernatant from whole blood collected without anticoagulants, allowed to clot (30 minutes) and centifuged to separate serum from the clotted blood. Serum does not contain clotting factors.
Solvent flush technique	Recommended manual gas chromatographic injection technique: 1. Flush syringe several times with solvent; 2. Draw into 10-µL syringe, in order: 3 µL solvent, 0.2 µL air, 5 µL sample, 1.2 µL air; and 3. Inject entire contents of syringe onto GC.
Spike	A known mass of analyte added to a sampler for the purpose of determining recovery (analyst spikes), or for quality control (blind spikes). Also see DE.
sp.gr.	Specific gravity, relative to water at the same temperature.
Spot sample (urine)	Urine sample collected at a specified time.
s_r	Estimate of the relative standard deviation, equal to s divided by the mean of a series of measurements. A measure of precision. Previously called CV (coefficient of variation).
STEL	Short-Term (15-min) Exposure Limit, used by the ACGIH TLV list (see TLV).
t	Temperature, °C; also time, min.
T_c	Temperature, kelvins (K), at which sampling pump was calibrated.
TEM	Transmission electron microscopy.
TLC	Thin-layer chromatography.
TLV	Threshold limit value, listed in TLVs, Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment with Intended Changes for 1983-84 (American Conference of Governmental Industrial Hygienists, Cincinnati, OH, 1983).
t_r	Retention time, min.
T_s	Temperature, kelvins (K), at which air sample was taken.
TWA	Time-weighted average.
User check	An evaluation of a written procedure for clarity and accuracy in which an independent laboratory analyzes a small number of spiked samples following the procedure exactly.

UV	Ultraviolet.
V	Volume of air sample, in L, as taken at the sampling site, corrected if necessary for rotameter calibration at a different temperature and pressure: $V = (\text{flow rate})(\text{time})(P_C\ T_S/P_S\ T_C)^{0.5}$ (see pages 18 and Appendix II (page A-2) for an example).
Validated method	A method which meets or exceeds certain sampling and measurement performance criteria; for example, the criteria given in Chapter E, "Development and Evaluation of Methods," and in references 1 through 5 of that chapter (page 34).
V_m	Volume of 1 mole of ideal gas at the specified temperature and pressure.
VOL-MAX	Maximum recommended air sample volume, L, based on sampler capacity or other limitation, @ OSHA PEL.
VOL-MIN	Minimum recommended air sample volume, L, based on an atmosphere at the OSHA PEL concentration and collecting a mass of substance which is equivalent to the lower end of the measurement range (q.v.).
VP	Vapor pressure.
W	Mass of analyte found on an exposed single-section sampler (e.g., membrane filter).
W_b	Mass of analyte found on the back section of an exposed sampler.
W_f	Mass of analyte found on the front section of an exposed sampler.
Working range	Range of air concentrations, in ppm or mg/m^3, extending from the LOQ to a maximum determined by sampler capacity or measurement considerations.
XRD	X-ray diffraction.
XRF	X-ray fluorescence.

V. A. INDEX OF THIRD EDITION METHOD NUMBERS

3rd ed. Method Number	Substance
0500	Nuisance dust, total
0600	Nuisance dust, respirable
1000	Allyl chloride
1002	Chloroprene
1003	Hydrocarbons, Halogenated I:
	Benzyl chloride
	Bromoform
	Carbon tetrachloride
	Chlorobenzene
	Chlorobromomethane
	Chloroform
	o-Dichlorobenzene
	p-Dichlorobenzene
	1,1-Dichloroethane
	1,2-Dichloroethylene
	Ethylene dichloride
	Hexachloroethane
	Methyl chloroform
	Propylene dichloride
1004	sym-Dichloroethyl ether
1005	Methylene chloride
1007	Vinyl chloride
1008	Ethylene dibromide
1009	Vinyl bromide
1010	Epichlorohydrin
1300	Ketones I:
	Acetone
	Cyclohexanone
	Diisobutyl ketone
	2-Hexanone
	Hexone
	2-Pentanone
1301	Ketones II:
	Camphor
	Ethyl butyl ketone
	Mesityl oxide
	Methyl (n-amyl) ketone
	5-Methyl-3-heptanone
1400	Alcohols I:
	tert-Butyl alcohol
	Ethanol
	Isopropyl alcohol
1401	Alcohols II:
	n-Butyl alcohol
	sec-Butyl alcohol
	Isobutyl alcohol
	n-Propyl alcohol

3rd ed. Method Number	Substance
1402	Alcohols III:
	Allyl alcohol
	Cyclohexanol
	Diacetone alcohol
	Isoamyl alcohol
	Methyl isobutyl carbinol
1403	Alcohols IV:
	2-Butoxyethanol
	2-Ethoxyethanol
	Methyl cellosolve
1450	Esters I:
	n-Amyl acetate
	sec-Amyl acetate
	n-Butyl acetate
	sec-Butyl acetate
	tert-Butyl acetate
	2-Ethoxyethyl acetate
	Ethyl acrylate
	Isoamyl acetate
	Isobutyl acetate
	Methyl isoamyl acetate
	n-Propyl acetate
1500	Hydrocarbons, BP 36 - 126 °C:
	Benzene
	Cyclohexane
	Cyclohexene
	Heptane
	Hexane
	Methylcyclohexane
	Octane
	Pentane
	Toluene
1501	Hydrocarbons, aromatic:
	Benzene
	p-tert-Butyl toluene
	Cumene
	Ethylbenzene
	α-Methylstyrene
	Naphthalene
	Styrene
	Toluene
	Vinyl toluene
	Xylene

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3rd ed. Method Number	Substance
1550	Naphthas:
	Naphtha, coal tar
	Naphtha, petroleum
	Stoddard solvent
1551	Turpentine
1600	Carbon disulfide
1601	1,1-Dichloro-1-nitroethane
1603	Acetic acid
1604	Acrylonitrile
1606	Acetonitrile
2000	Methanol
2001	Cresol
2500	2-Butanone
2501	Acrolein
2502	Formaldehyde (oxazolidine)
2503	Mevinphos (Phosdrin)
2504	Tetraethyl pyrophosphate
2507	Nitroglycerin/EGDN
2508	Isophorone
2510	1-Octanethiol
3500	Formaldehyde (chromotropic acid)
3501	Formaldehyde (Girard T)
3502	Phenol
3503	Hydrazine
5000	Carbon black
5001	2,4-D and 2,4,5-T
5002	Warfarin
5003	Paraquat
5004	Hydroquinone
5005	Thiram
5006	Carbaryl (Sevin)
5007	Rotenone
5009	Benzoyl peroxide
5010	Bromoxynil and Bromoxynil octanoate
5011	Ethylene thiourea
5012	EPN, Malathion, and Parathion
5013	Dyes, benzidine, o-anisidine, and o-tolidine
5014	Chlorinated terphenyl
5500	Ethylene glycol
5502	Aldrin and Lindane
5503	Polychlorobiphenyls
5505	Isocyanate group
5508	Kepone
6000	Mercury
6600	Nitrous oxide
6700	Nitrogen dioxide
7013	Aluminum
7020	Calcium
7024	Chromium
7027	Cobalt
7029	Copper (fume and dust)
7030	Zinc
7048	Cadmium
7074	Tungsten (soluble/insoluble)
7082	Lead
7102	Beryllium
7200	Welding and brazing fume:
	Cadmium
	Chromium
	Copper
	Iron
	Manganese
	Nickel
	Silver
	Zinc
7300	Elements (ICP):
	Aluminum
	Arsenic
	Beryllium
	Cadmium
	Calcium
	Chromium
	Cobalt
	Copper
	Iron
	Lead
	Lithium
	Magnesium
	Manganese
	Molybdenum
	Nickel
	Phosphorus
	Platinum
	Selenium
	Silver
	Sodium
	Tellurium
	Thallium
	Tin
	Titanium
	Tungsten
	Vanadium
	Yttrium
	Zinc
	Zirconium
7400	Fibers (asbestos, etc.)
7401	Alkaline dusts

3rd ed. Method Number	Substance
7500	Silica, crystalline (XRD)
7501	Silica, amorphous
7502	Zinc oxide
7505	Lead sulfide
7600	Chromium, hexavalent
7601	Silica, crystalline (color)
7602	Silica, crystalline (IR)
7900	Arsenic (hydride AAS)
7901	Arsenic trioxide (graphite AAS)
7902	Fluorides (aerosol and gas)
7903	Acids, inorganic (IC):
	Hydrogen bromide
	Hydrogen chloride
	Hydrogen fluoride
	Nitric acid
	Phosphoric acid
	Sulfuric acid
7904	Cyanides (aerosol and gas)
8000	ALAD in blood
8001	Pentachlorophenol in blood
8002	2-Butanone, ethanol, and toluene in blood
8003	Lead in blood and urine
8004	PCB in blood
8300	Hippuric acid in urine (color)
8301	Hippuric and methyl hippuric acids in urine (HPLC)
8302	MBOCA in urine
8303	Pentachlorophenol in urine
8304	Benzidine in urine (TLC)
8306	Benzidine in urine (GC)
8308	Fluoride in urine
8310	Metals in urine:
	Aluminum
	Barium
	Cadmium
	Chromium
	Copper
	Iron
	Lead
	Manganese
	Molybdenum
	Nickel
	Platinum
	Silver
	Strontium
	Tin
	Titanium
	Zinc
9000	Chrysotile asbestos (bulk)

V. B. INDEX OF SECOND EDITION METHOD NUMBERS

(The Second Edition Method Number is the method number as it appeared in the indicated volume of the NIOSH Manual of Analytical Methods, 2nd Edition, Vols. 1 through 7).

CRDT = Criteria Document

SDS = Sampling Data Sheet from NIOSH Publication 77-159

NR = Not revised

TBR = To be revised by June, 1985

2nd Ed. Method Number	2nd Ed. Vol. Number	Substance	3rd Ed. Method Number	Alternate Methods
P&CAM102	1	Lead in blood (Dithizone)	NR	8003
106	1	Silica (colorimetric)	7601	
107	1	Antimony in urine	TBR	
108	1	Nitrogen oxides	NR	6700
109	1	Silica (XRD)	NR	7500
110	1	Silica (Infrared)	7602	
112	1	Carbon monoxide	TBR	
113	1	Carbon monoxide in blood	NR	
114	1	Fluoride in urine	8308	
115	1	Hydrogen chloride	NR	7903
116	1	Cyanide	7904	
117	1	Hydrogen fluoride	NR	7902 or 7903
118	1	Acrolein	NR	2501
121	1	Beryllium	NR	7102 or 7300
124	1	Selenium in urine	TBR	
125	1	Formaldehyde	3500	2502 or 3501
126	1	Hydrogen sulfide	TBR	
127	1	Acetone	1300	
127	1	Benzene	1500, 1501	
127	1	2-Butanone	2500	
127	1	Carbon tetrachloride	1003	
127	1	Chloroform	1003	
127	1	p-Dioxane	TBR	
127	1	Ethylene dichloride	1003	
127	1	Methyl chloroform	1003	
127	1	Methylene chloride	1005	
127	1	Styrene	1501	
127	1	Tetrachloroethylene	TBR	
127	1	Toluene	1500, 1501	
127	1	1,1,2-Trichloroethane	TBR	
127	1	Trichloroethylene	TBR	
127	1	Xylene	1501	
139	1	Arsenic	7900	7300 or 7901
139	1	Arsenic in urine	TBR	
140	1	Arsenic in urine	NR	
141	1	TDI	NR	
142	1	MDI	NR	
145	1	Mercury in urine	NR	
146	1	Sulfur dioxide	TBR	

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2nd Ed. Method Number	2nd Ed. Vol. Number	Substance	3rd Ed. Method Number	Alternate Methods
P&CAM152	1	Chromium	7024	7300
153	1	Ozone	NR	
154	1	Ozone	NR	
158	1	Parathion	NR	5012
159	1	Oil mist	TBR	
160	1	Sulfur dioxide	TBR	
163	1	Sulfur dioxide	NR	
165	1	Mercury in urine	TBR	
167	1	Mercury in blood	NR	
168	1	Aniline	TBR	
168	1	o-Toluidine	TBR	
168	1	Xylidine	TBR	
169	1	Chromic acid	7600	
173	1,5	Aluminum	7013	7300
173	1	Antimony	NR	
173	1,5	Arsenic	NR	7300, 7900 or 7901
173	1,5	Barium	TBR	
173	1,5	Beryllium	NR	7102 or 7300
173	1,5	Bismuth	TBR	
173	1,5	Cadmium	7048	7300
173	1,5	Calcium	7020	7300
173	1,5	Chromium	7024	7300
173	1,5	Cobalt	7027	7300
173	1,5	Copper	7029	7300
173	1,5	Indium	TBR	
173	1,5	Iron	TBR	7300
173	1,5	Lead	7082	7300
173	1,5	Lithium	TBR	7300
173	1,5	Magnesium	TBR	7300
173	1,5	Manganese	TBR	7300
173	1,5	Molybdenum	TBR	7300
173	1,5	Nickel	TBR	7300
173	1,5	Palladium	TBR	
173	1,5	Potassium	TBR	
173	1,5	Rubidium	TBR	
173	1,5	Silicon	NR	7300
173	1,5	Silver	NR	7300
173	1,5	Sodium	TBR	7300
173	1,5	Strontium	TBR	
173	1,5	Tellurium	TBR	7300
173	1,5	Thallium	TBR	7300
173	1,5	Vanadium	NR	7300
173	1,5	Zinc	7030	7300
175	5	Mercury	6000	
176	1	Tin	TBR	7300
177	1	Gallium	NR	
178	1	Vinyl chloride	1007	
179	1	Carbon disulfide	NR	1600

2nd Ed. Method Number	2nd Ed. Vol. Number	Substance	3rd Ed. Method Number	Alternate Methods
P&CAM 180	1	Arsenic	NR	7300, 7900 or 7901
181	1	Selenium	NR	7300
182	1	Chromium	NR	7024, 7300 or 7600
183	1	Polynuclear aromatic hydrocarbons	TBR	
184	1	Polynuclear aromatic hydrocarbons	TBR	
186	1	Polynuclear aromatic hydrocarbons	TBR	
187	1	Sulfuric acid	NR	7903
188	1	Arsenic	NR	7300, 7900 or 7901
189	1	Antimony	NR	
190	1	Indium	NR	
191	1	Cadmium	NR	7048 or 7300
191	1	Lead	NR	7082 or 7300
192	1	Arsenic in blood	NR	
193	1	Antimony in blood	NR	
194	1	Indium in blood	NR	
195	1	Lead in blood	NR	8003
196	1	Arsenic in urine	NR	
197	1	Antimony in urine	NR	
198	1	Gallium in urine	NR	
199	1	Indium in urine	NR	
200	1	Lead in urine	NR	8003 or 8310
201	1	Methyl chloride	1001	
202	1	Acrylonitrile	NR	1604
203	1	Nitroglycerin/EGDN	2507	
204	1	Sulfur dioxide	NR	
205	1	Ammonia	TBR	
206	1	Polynuclear aromatic hydrocarbons	TBR	
208	1	Lead in blood and urine	8003	8310
209	1	Chlorine	NR	
211	1	Acrolein	NR	2501
212	1	Fluorides	7902	7903
213	1	bis-(Chloromethyl)ether	NR	
214	1	Lead in air or blood	NR	7082, 7300 or 8003
215	1	Phosphate in urine	TBR	
216	1	Phosphoric acid	NR	7903
217	1	Benzene solubles	TBR	
219	1	Phosgene	NR	
220	1	Chloromethyl methyl ether	NR	
221	1	Aliphatic amines	TBR	
222	1	Zinc oxide	7502	
223	1	Cadmium in blood	NR	
224	1	Cadmium in urine	NR	8310
225	1	Kepone	5508	
226	1	2,6-Di-t-butyl-p-cresol	TBR	
227	1	Polymethylsiloxane	TBR	
228	1	Thiram	5005	
230	1	Pentachlorophenol in urine	8303	
231	1	Nitrogen oxides	6700	

2nd Ed. Method Number	2nd Ed. Vol. Number	Substance	3rd Ed. Method Number	Alternate Methods
P&CAM232	1	Formic acid	TBR	
234	1	Dyes, benzidine, o-tolidine	NR	5013
235	1	Formaldehyde	NR	2502, 3500, or 3501
236	1	MOCA	TBR	
237	1	Tissue preparation	NR	
239	1	Asbestos	7400	
241	1	Sodium hydroxide	7401	
242	1	Phosphorus	NR	
243	1	Benzidine	TBR	
244	1	Polychlorinated biphenyls	5503	
245	1	Asbestos (chrysotile, bulk)	NR	7400
246	1	3,3'-Dichlorobenzidine	TBR	
247	1	Methanol	2000	
248	1	1,1-Dimethyl hydrazine	TBR	
248	1	Hydrazine	TBR	3503
248	1	Methyl hydrazine	TBR	
248	1	Phenyl hydrazine	TBR	
250	4	Zirconium oxide	TBR	
251	1	Benzo(a)pyrene	TBR	
252	1	Dimethylnitrosamine		
253	1	Polychlorinated biphenyls	5503	
255	1	Thiophene	TBR	
256	1	Azelaic acid	TBR	
257	1	Phosphorus	TBR	
259	1,5	Silica, crystalline	7500	7601 or 7602
260	4	Ethylene dibromide	1008	
261	4	Antimony	TBR	
262	1	Lead in blood and urine	8003	8310
263	4	Hexamethylenetetramine	TBR	
264	4	Naphthylamines	TBR	
265	4	Arsine	TBR	
266	4	Vinylidene chloride	TBR	
267	5	Sulfuric acid	NR	7903
268	5	Sulfur dioxide, sulfates, sulfites	TBR	
269	4	4-Aminobiphenyl	TBR	
270	4	Aminoethanol compounds	TBR	
271	4	Tungsten	7074	7300
272	4	2-Nitropropane	TBR	
273	4	4-Nitrobiphenyl	TBR	
276	4	Ethylenediamine	TBR	
277	4	Methylamine	TBR	
278	4	Vinyl acetate	TBR	
279	4	Beryllium in tissue	NR	
280	4	N,N-Dimethyl-p-toluidine	TBR	
281	4	Ethylene thiourea	5011	
282	4	Tetramethyl thiourea	TBR	
283	4	Oil mist	TBR	
284	4	4-Dimethylaminoazobenzene	TBR	

2nd Ed. Method Number	2nd Ed. Vol. Number	Substance	3rd Ed. Method Number	Alternate Methods
P&CAM285	5	Crotonaldehyde	TBR	
286	5	Arsenic	7901	7300 or 7900
288	5	Beryllium	7102	7300
290	5	Vanadium	TBR	7300
291	5	α-chloroacetophenone	NR	
294	5	Cyclopentadiene	TBR	
295	5	Dichlorovos	TBR	
296	6	Hydrogen sulfide	TBR	
297	5	Dibutyl phosphate	TBR	
298	5,7	Nickel	TBR	7300
299	5	Dimethylnitrosamine	TBR	
300	5	Ethylenimine (aziridine)	TBR	
301	5	Dimethyl sulfate	TBR	
302	5	Maleic anhydride	TBR	
303	5	Styrene oxide	TBR	
304	5	OCBM	TBR	
305	5	Phosphorus trichloride	TBR	
307	5	Hexachlorobutadiene	TBR	
308	5	Hexachlorocyclopentadiene	TBR	
309	5	Chrysotile asbestos (bulk)	9000	
310	5	Hydrogen chloride	7903	
313	6	Warfarin	5002	
314	5	Trichloroisocyanuric acid	TBR	
315	5	Benzidine in urine	8304	8306
316	6	Silica, amorphous	7501	
317	6	Diethylcarbamoyl chloride	TBR	
318	6	Formaldehyde	NR	2502, 3500, or 3501
319	6	Chromium (VI)	7600	
320	6	Arsenic, organo-	TBR	
321	6	1,2-Dichloroproane	TBR	
322	6	Trimellitic anhydride	TBR	
323	6	Titanium diboride	TBR	
324	6	Boron carbide	TBR	
325	6	Benzidine, o-anisidine, and o-tolidine dyes	5013	
326	6	TDI	NR	
327	6	Hippuric acid in urine	8300	
328	6	ALAD in blood	8000	
329	6	PCB in blood	8004	
330	6	Phenol and Cresol in urine	TBR	
331	6	Methyl ethyl ketone peroxide	TBR	
332	6	Chloroacetic acid	TBR	
333	6	Bisphenol A	TBR	
335	6	Pentachloroethane	TBR	
336	6	Tetraethyl pyrophosphate	2504	
337	7	p-Chlorophenol	TBR	
338	7	Ethylene glycol	5500	
339	7	Inorganic acids	7903	

2nd Ed. Method Number	2nd Ed. Vol. Number	Substance	3rd Ed. Method Number	Alternate Methods
P&CAM340	7	Acetone cyanohydrin	TBR	
341	7	Diborane	TBR	
342	7	MOCA in urine	8302	
343	7	Polychlorobenzenes	TBR	
344	7	Nickel carbonyl	TBR	
345	7	Welding and brazing fume	7200	
346	7	Arsenic	7901	7300 or 7900
347	7	MDI	NR	
348	7	2,4,7-Trinitro-9-fluorenone	TBR	
349	7	Vinyl bromide	1009	
350	7	Lead sulfide	7505	
351	7	Elements by ICP	7300	
354	7	Formaldehyde	2502	3500 or 3501
355	—	Talc, respirable	TBR	
357	—	n-Octanethiol	2510	
358	—	Pentachlorophenol in blood	8001	
359	—	Benzidine in urine	8306	
360	—	Hippuric Acid in urine	8300	8301
361	—	2-Butanone, ethanol, and toluene in blood	8002	
362	—	Pentachlorophenol in urine	8303	
363	—	Polychlorinated terphenyls	5014	
364	—	Vanadium oxides	TBR	7300
365	—	2-Butanone	2500	8002
368	—	Tin, organo-	TBR	
374	—	Acrolein	2501	
S1	2	Acetone	1300	
S2	2	Antimony	NR	
S3	2	2-Butanone	2500	
S4	2	Hydrogen sulfide	TBR	
S5	2	Manganese	TBR	7300
S7	5	p-Nitroaniline	TBR	
S8	2	Ozone	NR	
S10	2	Camphor	1301	
S11	5	Chloroacetaldehyde	TBR	
S12	2	Mesityl oxide	1301	
S13	2	5-Methyl-3-heptanone	1301	
S15	2	Methyl (n-amyl) ketone	1301	
S16	2	Ethyl butyl ketone	1301	
S17	5	Furfural	TBR	
S18	2	Hexone	1300	
S19	2	Cyclohexanone	1300	
S20	2	2-Pentanone	1300	
S22	2	p-tert-Butyltoluene	1501	
S23	2	Cumene	1501	
S24	4	Diphenyl	TBR	
S25	2	Vinyl toluene	1501	
S26	2	α-Methyl styrene	1501	

2nd Ed. Method Number	2nd Ed. Vol. Number	Substance	3rd Ed. Method Number	Alternate Methods
S27	2	Terphenyl	TBR	
S28	2	Cyclohexane	1500	
S29	2	Ethylbenzene	1501	
S30	2	Styrene	1501	
S31	2	sec-amyl Acetate	1450	
S32	2	tert-Butyl acetate	1450	
S33	2	Dibutyl phthalate	TBR	
S35	2	Ethyl acrylate	1450	
S36	2	Ethyl formate	TBR	
S37	2	Methyl isoamyl acetate	1450	
S38	2	Methyl acrylate	TBR	
S39	2	Methyl cellosolve acetate	TBR	
S40	2	Di-2-ethylhexyl phthalate	TBR	
S41	2	2-Ethoxyethyl acetate	1450	
S42	2	Methyl acetate	TBR	
S43	6	Methyl methacrylate	TBR	
S44	2	Isobutyl acetate	1450	
S45	2	Isoamyl acetate	1450	
S46	2	sec-Butyl acetate	1450	
S47	2	n-Butyl acetate	1450	
S48	2	n-Propyl acetate	1450	
S49	2	Ethyl acetate	TBR	
S50	2	Isopropyl acetate	TBR	
S51	2	n-amyl Acetate	1450	
S52	2	Allyl alcohol	1402	
S53	2	sec-Butyl alcohol	1401	
S54	2	Cyclohexanol	1402	
S55	2	Diacetone alcohol	1402	
S56	2	Ethanol	1400	
S57	2	Hydroquinone	5004	
S58	2	Isoamyl alcohol	1402	
S59	2	Methanol	2000	
S60	2	Methyl isobutyl carbinol	1402	
S62	2	n-Propyl alcohol	1401	
S63	2	tert-Butyl alcohol	1400	
S64	2	Isobutyl alcohol	1401	
S65	2	Isopropyl alcohol	1400	
S66	2	n-Butyl alcohol	1401	
S67	2	Chlorinated camphene	TBR	
S69	2	Dipropylene glycol methyl ether	1605	
S70	2	Glycidol	TBR	
S71	2	Methylal	TBR	
S72	2	Phenyl ether	TBR	
S73	2	Phenyl ether-biphenyl mixture	TBR	
S74	2	Phenyl glycidyl ether	TBR	
S75	2	Propylene oxide	TBR	
S76	2	2-Butoxyethanol	1403	
S77	2	Isopropyl glycidyl ether	TBR	

2nd Ed. Method Number	2nd Ed. Vol. Number	Substance	3rd Ed. Method Number	Alternate Methods
S78	2	Tetrahydrofuran	TBR	
S79	2	Methyl cellosolve	1403	
S80	2	Ethyl ether	TBR	
S81	2	n-Butyl glycidyl ether	TBR	
S82	2	Cyclohexene	1500	
S84	5	Methyl acetylene	TBR	
S85	6	Methyl acetylene/propadiene	TBR	
S86	2	Naphtha, coal tar	1550	
S87	2	Propane	TBR	
S88	2	Turpentine	1551	
S89	2	Heptane	1500	
S90	2	Hexane	1500	
S91	2	Butadiene	TBR	
S92	2	Ketene	TBR	
S93	2	LPG	TBR	
S94	2	Methylcyclohexane	1500	
S95	2	Propylene dichloride	1003	
S96	2	Pentachloronaphthalene	NR	
S97	2	Octachloronaphthalene	TBR	
S98	2	Methyl iodide	TBR	
S99	4	Methyl chloride	TBR	
S100	2	Hexachloronaphthalene	TBR	
S101	2	Hexachloroethane	1003	
S102	2	Fluorotrichloromethane	TBR	
S103	2	Ethylene chlorohydrin	TBR	
S104	2	Ethylene dibromide	1008	
S105	4	Ethyl chloride	TBR	
S106	2	Ethyl bromide	TBR	
S107	2	Difluorodibromomethane	TBR	
S108	2	Dichlorotetrafluoroethane	TBR	
S109	2	Dichloromonofluoromethane	TBR	
S110	2	1,2-Dichloroethylene	1003	
S111	2	Dichlorodifluoromethane	TBR	
S112	2	Chloroprene	1002	
S113	2	Chlorobromomethane	1003	
S114	2	Bromoform	1003	
S115	2	Benzyl chloride	1003	
S116	2	Allyl chloride	1000	
S117	2	Acetylene tetrabromide	TBR	
S118	2	Epichlorohydrin	1010	
S119	2	Chlorinated diphenyl oxide	TBR	
S120	4	Polychlorinated biphenyls	5503	
S121	2	Polychlorinated biphenyls	NR	
S122	2	Ethylene dichloride	1003	
S123	2	1,1-Dichloroethane	1003	
S124	2	1,1,2,2-Tetrachloroethane	TBR	
S125	2	Trifluorobromomethane	TBR	
S126	2	1,2,3-Trichloropropane	TBR	

2nd Ed. Method Number	2nd Ed. Vol. Number	Substance	3rd Ed. Method Number	Alternate Methods
S128	2	Trichloronaphthalene	NR	
S129	2	1,1,2-Trichloro-1,2,2-trifluoroethane	TBR	
S130	2	Tetrachloronaphthalene	NR	
S131	2	1,1,1,2-Tetrachlorodifluoroethane	TBR	
S132	2	1,1,2,2-Tetrachlorodifluoroethane	TBR	
S133	2	Chlorobenzene	1003	
S134	2	1,1,2-Trichloroethane	TBR	
S135	3	o-Dichlorobenzene	1003	
S137	3	Diazomethane	TBR	
S138	4	n-Butylamine	TBR	
S139	3	Diethylamine	TBR	
S140	5	Diethylaminoethanol	TBR	
S141	4	Diisopropylamine	TBR	
S142	3	Dimethylamine	TBR	
S143	3	1,1-Dimethyl hydrazine	TBR	
S144	3	Ethylamine	TBR	
S146	3	N-Ethyl morpholine	TBR	
S147	3	Isopropylamine	TBR	
S148	6	Methylamine	TBR	
S149	3	Methyl hydrazine	TBR	
S150	3	Morpholine	TBR	
S152	3	Triethylamine	TBR	
S153	3	Monomethylaniline	TBR	
S155	3	Tetramethylsuccinonitrile	TBR	
S156	3	Acrylonitrile	1604	
S158	4	2-Aminopyridine	TBR	
S160	3	Phenyl hydrazine	TBR	
S161	3	Pyridine	TBR	
S162	3	Xylidine	TBR	
S163	5	Anisidine	TBR	
S164	3	Dimethylaniline	TBR	
S165	3	Acetonitrile	1606	
S166	5	Dinitro-o-cresol	TBR	
S167	3	Cresol	2001	
S168	3	o-Toluidine	TBR	
S169	4	Acetic acid	1603	
S170	3	Acetic anhydride	TBR	
S173	5	Formic acid	TBR	
S174	3	Sulfuric acid	NR	7903
S175	3	Hydrogen bromide	NR	7903
S176	3	Hydrogen fluoride	NR	7902 or 7903
S178	3	2-Hexanone	1300	
S179	3	Phthalic anhydride	TBR	
S181	4	Quinone	TBR	
S182	5	Silver	7300	
S183	3	Tin	TBR	7300
S185	3	Zirconium	TBR	7300

2nd Ed. Method Number	Vol. Number	Substance	3rd Ed. Method Number	Alternate Methods
S186	3	Copper	7029	7300
S187	3	Tellurium hexafluoride	TBR	
S188	3	Rhodium, fume and dust	TBR	
S189	3	Rhodium, soluble	TBR	
S190	3,7	Selenium	TBR	7300
S191	3,7	Platinum	TBR	7300
S193	3	Molybdenum	TBR	7300
S194	5	Hafnium	TBR	
S198	3	Barium	TBR	
S199	4	Mercury	6000	
S200	3	Yttrium	TBR	7300
S201	5	Tantalum	7300	
S203	4	Cobalt	7027	7300
S204	3,7	Tellurium	TBR	7300
S205	3	Calcium	7020	7300
S206	3	Nickel	TBR	7300
S208	3	Tributyl phosphate	TBR	
S209	3	Triorthocresyl phosphate	TBR	
S210	3	Triphenyl phosphate	TBR	
S211	5	1-Chloro-1-nitropropane	TBR	
S213	3	1,1-Dichloro-1-nitroethane	1601	
S214	4	Dinitrobenzene	TBR	
S215	4	Dinitrotoluene	TBR	
S216	3	Nitroglycerin/EGDN	2507	
S217	3	Nitrobenzene	TBR	
S218	3	p-Nitrochlorobenzene	TBR	
S219	4,6	Nitroethane	TBR	
S220	6	Nitromethane	TBR	
S223	3	Nitrotoluene	TBR	
S224	3	Tetranitromethane	NR	
S225	3	Tetryl	TBR	
S227	3	n-Propyl nitrate	TBR	
S228	4	Picric acid	TBR	
S229	3	Arsine	TBR	
S237	3	Hydrazine	3503	
S243	4	Stibine	TBR	
S244	5	Sulfur hexafluoride	TBR	
S245	6	Sulfuryl fluoride	TBR	
S246	3	Hydrogen chloride	NR	7903
S248	3	Carbon disulfide	1600	
S249	3	Carbon dioxide	TBR	
S250	3	Cyanide	7904	
S253	4	Benzoyl peroxide	5008	
S254	3	Dimethyl acetamide	TBR	
S255	3	Dimethyl formamide	TBR	
S256	5	Thiram	5005	
S257	5	Phosphorus pentachloride	TBR	
S262	3	Carbon black	5000	
S264	3	Ethyl silicate	TBR	

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S274	3	DDT	TBR	
S275	3	Aldrin	5502	
S276	5	ANTU	TBR	
S278	6	Chlordane	TBR	
S279	5	2,4-D	5001	
S280	6	Demeton	TBR	
S281	3	p-Dichlorobenzene	1003	
S283	3	Dieldrin	TBR	
S284	6	Endrin	TBR	
S285	3	EPN	5012	
S286	3	Ethylene oxide	TBR	
S287	5	Heptachlor	TBR	
S288	4	Hydrogen cyanide	7904	
S290	3	Lindane	5502	
S291	5	Methyl formate	TBR	
S292	3	Naphthalene	1501	
S293	3	Nicotine	TBR	
S294	5	Paraquat	5003	
S295	3	Parathion	5012	
S296	6	Mevinphos (Phosdrin)	2503	
S297	4	Pentachlorophenol	TBR	
S298	6	Pyrethrum	TBR	
S299	6	Ronnel	TBR	
S300	5	Rotenone	5007	
S301	5	Sodium fluoroacetate	TBR	
S302	5	Strychnine	TBR	
S303	5	2,4,5-T	5001	
S306	3	Thallium	TBR	7300
S308	4	Sulfur dioxide	NR	
S309	3	Arsenic	7901	7300 or 7900
S310	3	Aniline	TBR	
S311	3	Benzene	1500, 1501	
S312	3	Cadmium	7048	7300
S313	3	Cadmium fume	7048	7300
S314	3	Carbon tetrachloride	1003	
S315	3	Silica, crystalline	7500	7601 or 7602
S316	4	Zinc oxide	7502	
S317	3	Chromium, hexavalent	7600	
S318	3	Xylene	1501	
S319	4	Nitric acid	NR	7903
S320	4	Nitrogen dioxide	6700	
S321	4	Nitric oxide	TBR	
S323	3	Chromium	7024	7300
S327	4	Formaldehyde (Girard T)	3501	2502 or 3500
S328	3	Methyl chloroform	1003	

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S330	3	Phenol	3502	
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S333	3	Phosphoric acid	TBR	7903
S334	4	Phosphorus	TBR	7300
S335	3	Tetrachloroethylene	TBR	
S336	3	Trichloroethylene	TBR	
S339	3	Beryllium	7102	7300
S340	4	Carbon monoxide	TBR	
S341	3,7	Lead	7082	7300
S342	6	Mercury, organo	TBR	
S343	3	Toluene	1500, 1501	
S346	4	Allyl glycidyl ether	TBR	
S347	5	Ammonia	TBR	
S348	5	Ammonium sulfamate	TBR	
S349	3	Boron oxide	0500	
S350	4	n-Butyl mercaptan	TBR	
S351	3	Chloroform	1003	
S352	3	Chromium	7024	7300
S354	4	Copper fume	7029	7300
S356	5	Crag herbicide I	NR	
S357	3	sym-Dichloroethyl ether	1004	
S358	3	Diisobutyl ketone	1300	
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S375	4	Methylcyclohexanone	TBR	
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S379	3	Pentane	1500	
S380	3	Naphtha, petroleum	1550	
S381	4	Sodium hydroxide	7401	
S382	3	Stoddard solvent	1550	
S383	4	Tetraethyl lead	TBR	
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Chrysotile asbestos (bulk), 9000
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Diamine, see Hydrazine, 3503
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2,6-Dibromo-4-cyanophenyl octanoate, see Bromoxynil and Bromoxynil octanoate, 5010
1,2-Dibromoethane, see Ethylene dibromide, 1008
3,5-Dibromo-4-hydroxybenzonitrile, see Bromoxynil and Bromoxynil octanoate, 5010
1,2-Dichlorobenzene, see Hydrocarbons, halogenated, 1003
1,4-Dichlorobenzene, see Hydrocarbons, halogenated, 1003
o-Dichlorobenzene, see Hydrocarbons, halogenated, 1003
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1,1-Dichloroethane, see Hydrocarbons, halogenated, 1003
1,2-Dichloroethane, see Hydrocarbons, halogenated, 1003
1,2-Dichloroethene, see Hydrocarbons, halogenated, 1003
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1,2-Dichloroethylene, see Hydrocarbons, halogenated, 1003
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1,1-Dichloro-1-nitroethane, 1601
(2,4-Dichlorophenoxy) acetic acid, see 2,4-D and 2,4,5-T, 5001
1,2,Dichloropropane, see Hydrocarbons, halogenated, 1003
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Emery, see Nuisance dust, total, 0500; Nuisance dust, respirable, 0600

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Fibrous glass, see Nuisance dust, total, 0500; Fibers, 7400
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Fluorides (aerosol and gas), 7902
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Formaldehyde (chromotropic acid), 3500
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γ-Hexachlorocyclohexane, see Aldrin and Lindane, 5502
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Hydroquinone, 5004
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2-Imidazolidinethione, see Ethylene thiourea, 5011
Iron, see Welding and Brazing fume, 7200; Elements, 7300;
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Kaolin, see Nuisance dust, total, 0500; Nuisance dust, respirable, 0600
Kepone, 5508
Kerosene, see Naphthas, 1550
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Ketones I, 1300
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Laughing gas, see Nitrous oxide, 6600
Lead, 7082; also see Elements, 7300
Lead in blood and urine, 8003
Lead in urine, see Metals in urine, 8310; Lead in blood and urine, 8003
Lead sulfide, 7505
Limestone, see Nuisance dust, total, 0500; Nuisance dust, respirable, 0600; Calcium, 7020
Lindane, see Aldrin and Lindane, 5502
Lithium, see Elements, 7300
Lithium hydroxide, see Alkaline dusts, 7401
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Magnesite, see Nuisance dust, total, 0500; Nuisance dust, respirable, 0600; Calcium, 7020
Magnesium, see Elements, 7300
Malathion, see EPN, Malathion, and Parathion, 5012
Manganese, see Welding and Brazing fume, 7200; Elements, 7300;
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Marble, see Nuisance dust, total, 0500; Nuisance dust, respirable, 0600; Calcium, 7020
MBK, see Ketones I, 1300
MBOCA in urine, 8302
MDI, see Isocyanate group, 5505
MEK, see 2-Butanone, 2500
MEK in blood, see 2-Butanone, Ethanol, and Toluene in blood, 8002
1-Mercaptooctane, see 1-Octanethiol, 2510
Mercury, 6000
Mesityl oxide, see Ketones II, 1301
Metals in urine (ICP), 8310
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Methanal, see Formaldehyde (oxazolidine), 2502; (chromotropic acid), 3500; (Girard T), 3501
Methane carboxylic acid, see Acetic acid, 1603
Methanol, 2000
2-Methoxyethanol, see Alcohols IV, 1403
Methyl alcohol, see Methanol, 2000
Methyl-(n-amyl)-ketone, see Ketones II, 1301
Methylbenzene, see Hydrocarbons, aromatic, 1501; Hydrocarbons, BP 36-126 °C, 1500
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3-Methyl-1-butanol, see Alcohols III, 1402
Methyl n-butyl ketone, see Ketones I, 1300
Methyl Cellosolve, see Alcohols IV, 1403
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Methyl cyanide, see Acetonitrile, 1606
Methylcyclohexane, see Hydrocarbons, BP 36-126 °C, 1500
4,4'-Methylenebis (2-chloroaniline) in urine, see MBOCA in urine, 8302
4,4'-Methylenediphenyl isocyanate, see Isocyanate group, 5505
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(1-Methylethenyl)-benzene, see Hydrocarbons, aromatic, 1501
Methyl ethyl ketone, see 2-Butanone, 2500
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4-Methyl-3-penten-2-one, see Ketones II, 1301
2-Methylphenol, see Cresols, 2001
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2-Methyl-1-propanol, see Alcohols II, 1401
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Methyl propyl ketone, see Ketones I, 1300
Methylstyrene, see Hydrocarbons, aromatic, 1501
α-Methylstyrene, see Hydrocarbons, aromatic, 1501
Methylvinylbenzene, see Hydrocarbons, aromatic, 1501

Methyl viologen, see Paraquat, 5003
Mevinphos, 2503
MIBC, see Alcohols III, 1402
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Mineral spirits, see Naphthas, 1550
Mineral wool fiber, see Nuisance dust, total, 0500; Nuisance dust, respirable, 0600; Fibers, 7400
MOCA in urine, see MBOCA in urine, 8302
Molybdenum, see Elements, 7300
Molybdenum in urine, see Metals in urine, 8310
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Naphthalene, see Hydrocarbons, aromatic, 1501
1-Naphthalenol methylcarbamate, see Carbaryl, 5006
Naphthas (refined petroleum solvents), 1550
NG, see Nitroglycerin and Ethylene glycol dinitrate, 2507
Nickel, see Welding and Brazing fume, 7200; Elements, 7300
Nickel in urine, see Metals in urine, 8310
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Nitrogen dioxide, 6700
Nitrogen peroxide, see Nitrogen dioxide, 6700
Nitroglycerin and Ethylene glycol dinitrate, 2507
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Nuisance dust, respirable, 0600
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Octalene, see Aldrin and Lindane, 5502
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Pentaerythritol, see Nuisance dust, total, 0500; Nuisance dust, respirable, 0600
Penta in blood, see Pentachlorophenol in blood, 8001
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n-Pentane, see Hydrocarbons, BP 36-126 °C, 1500
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  O-ethyl O-p-nitrophenyl ester, see EPN, Malathion, and Parathion, 5012
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Phosphorothioic acid O,O-diethyl
  O-(4-nitrophenyl)ester, see EPN, Malathion, and Parathion, 5012
Phosphorus, see Elements, 7300
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Polychloroterphenyl, see Chlorinated terphenyl, 5014
Portland cement, see Nuisance dust, total, 0500; Nuisance dust, respirable, 0600
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1,2,3-Propanetriol trinitrate, see Nitroglycerin and Ethylene glycol dinitrate, 2507
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2-Propanone, see Ketones I, 1300
2-Propenal, see Acrolein, 2501
2-Propenenitrile, see Acrylonitrile, 1604
2-Propenoic acid ethyl ester, see Esters I, 1450
2-Propen-1-ol, see Alcohols III, 1402
n-Propyl acetate, see Esters I, 1450
n-Propyl alcohol, see Alcohols II, 1401
Propylene dichloride, see Hydrocarbons, halogenated, 1003
Prussic acid, see Cyanides, 7904
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Rotenone, 5007
Rouge, see Nuisance dust, total, 0500; Nuisance dust, respirable, 0600
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Sevin, see Carbaryl, 5006
Silica, crystalline (XRD), 7500
Silica, crystalline (color), 7601
Silica, crystalline (IR), 7602
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Silicon carbide, see Nuisance dust, total, 0500; Nuisance dust, respirable, 0600
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Silver in urine, see Metals in urine, 8310

Sodium fluoride, see Fluorides, 7902
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Starch, see Nuisance dust, total, 0500; Nuisance dust, respirable, 0600
Stoddard solvent, see Naphthas, 1550
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2,4,5-T, see 2,4-D and 2,4,5-T, 5001
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Tin, see Elements, 7300
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Titanium, see Elements, 7300
Titanium in urine, see Metals in urine, 8310
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o-Tolidine, see Dyes, 5013
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Toluene in blood, see 2-Butanone, Ethanol, and Toluene in blood, 8002
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1,1,1-Trichloroethane, see Hydrocarbons, halogenated, 1003
Trichloromethane, see Hydrocarbons, halogenated, 1003
(2,4,5-Trichlorophenoxy) acetic acid, see 2,4-D and 2,4,5-T, 5001
Tridymite, see Silica, crystalline (XRD), 7500; (color), 7601; (IR), 7602
3,3,5-Trimethyl-2-cyclohexen-1-one, see Isophorone, 2508
Tubatoxin, see Rotenone, 5007
Tungsten (soluble and insoluble), 7074; also see Elements, 7300
Turpentine, 1551

Vanadium, see Elements, 7300
Vegetable oil mists (except castor, cashew nut, or similar irritant oils), see Nuisance dust, total, 0500; Nuisance.dust, respirable, 0600
Vinylbenzene, see Hydrocarbons, aromatic, 1501
Vinyl bromide, 1009
Vinyl chloride, 1007
Vinyl cyanide, see Acrylonitrile, 1604
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Zincite, see Zinc oxide, 7502
Zinc oxide, 7502; also see Nuisance dust, total, 0500; Nuisance dust, respirable, 0600; Zinc, 7030
Zinc stearate, see Nuisance dust, total, 0500; Nuisance dust, respirable, 0600
Zinc white, see Zinc oxide, 7502
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Zinc in urine, see Metals in urine, 8310
Zincite, see Zinc oxide, 7502
Zinc oxide, 7502; also see Nuisance dust, total, 0500; Nuisance dust, respirable, 0600; Zinc, 7030
Zinc stearate, see Nuisance dust, total, 0500; Nuisance dust, respirable, 0600
Zinc white, see Zinc oxide, 7502
Zirconium, see Elements, 7300

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