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Sampling and Analytical Procedures for the Industrial Hygiene Characterization of Coal Gasification and Liquefaction Pilot Plants

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SAMPLING AND ANALYTICAL PROCEDURES FOR THE INDUSTRIAL HYGIENE CHARACTERIZATION OF COAL GASIFICATION AND LIQUEFACTION PILOT PLANTS

I. INTRODUCTION

Coal gasification and liquefaction pilot plants are highly integrated operations processing a complex material, usually in a crowded environment. No two processes are the same, though unit operations may be similar from one plant to the next. General industrial hygiene sampling and analytical procedures for potentially hazardous emissions have not yet been comprehensively addressed. Although parts of such procedures have been used for other industrial hygiene studies of coal-derived materials, no real attempt has been made to deal with the complex modern coal conversion plant.

This report describes industrial hygiene sampling and analytical procedures that have been adapted to coal conversion facilities. These procedures, which are a synthesis of new and old techniques, are designed for potentially hazardous substances believed to be present in coal conversion facilities. It has not been practical to carry out all of these procedures at each facility because of cost constraints. Therefore a program has been designed in meetings with National Institute for Occupational Safety and Health (NIOSH) personnel, ranking the toxic substances according to hazard and available sampling and analytical procedures. This program allows for the judicious selection of substances to be sampled for and analyzed while still maintaining the objectives of the coal liquefaction and gasification industrial hygiene projects. It must be emphasized that industrial hygiene sampling and analysis in coal conversion plants is an emerging discipline and is still adopting and refining techniques. New procedures may be added to this protocol, as required, or the procedures described may be altered if this is justified by experience.

II. INDUSTRIAL HYGIENE SAMPLING PROCEDURE

A. SITE VISIT PREPARATION

Each sampling pump is identified by a four-digit number. For coal conversion projects, the number of each device used in each survey is recorded on the individual sampling data sheet. Enviro has in stock five critical orifices that have been calibrated with a two-stage cassette (Figure 1) in line using a dry test meter. A typical calibration curve for these orifices is shown in Figure 2. The figure shows that critical flow in the five orifices is reached at a minimum pressure of about 16 mm Hg, at which point the measured flow was 9.0 liters/min for two orifices and 9.2 liters/min for the remaining orifices. Typical runs with high-volume air-driven pumps at three different plants maintained minimal pressures of 25 mm Hg, which is well above the critical point of 16 mm Hg.

The two-stage sampling cassette used with the orifices (Figure 1) for sampling polynuclear aromatics (PNAs) is 37 mm in diameter and consists of a silver-membrane filter backed by a stainless-steel screen and Chromosorb 102 adsorbent. The use of Chromosorb 102 was recommended by our consultant, who has extensive experience in this type of sampling; the use of the silver membrane is based on the NIOSH standard method for sampling benzene-soluble substances. The filter and adsorbent are prewashed at the University of Iowa State Hygiene Laboratory (SHL), using repeated 12-hour Sohxlet extractions with methanol and methylene chloride until the wash extract is clean when injected into a gas chromatograph/mass spectrometer. The filter is dried at SHL and sent to Enviro. The adsorbent is shipped to Enviro in the extracting solution and is stored in the solution until needed, to minimize potential contamination; it is dried with nitrogen before use. The two-stage cassette is preassembled at Enviro with shrink bands to prevent leakage and contamination of the filter and adsorbent.

Enviro uses high-flow pumps for personal monitoring for PNAs and for particulate and trace-metal sampling. In personal monitoring for PNAs the

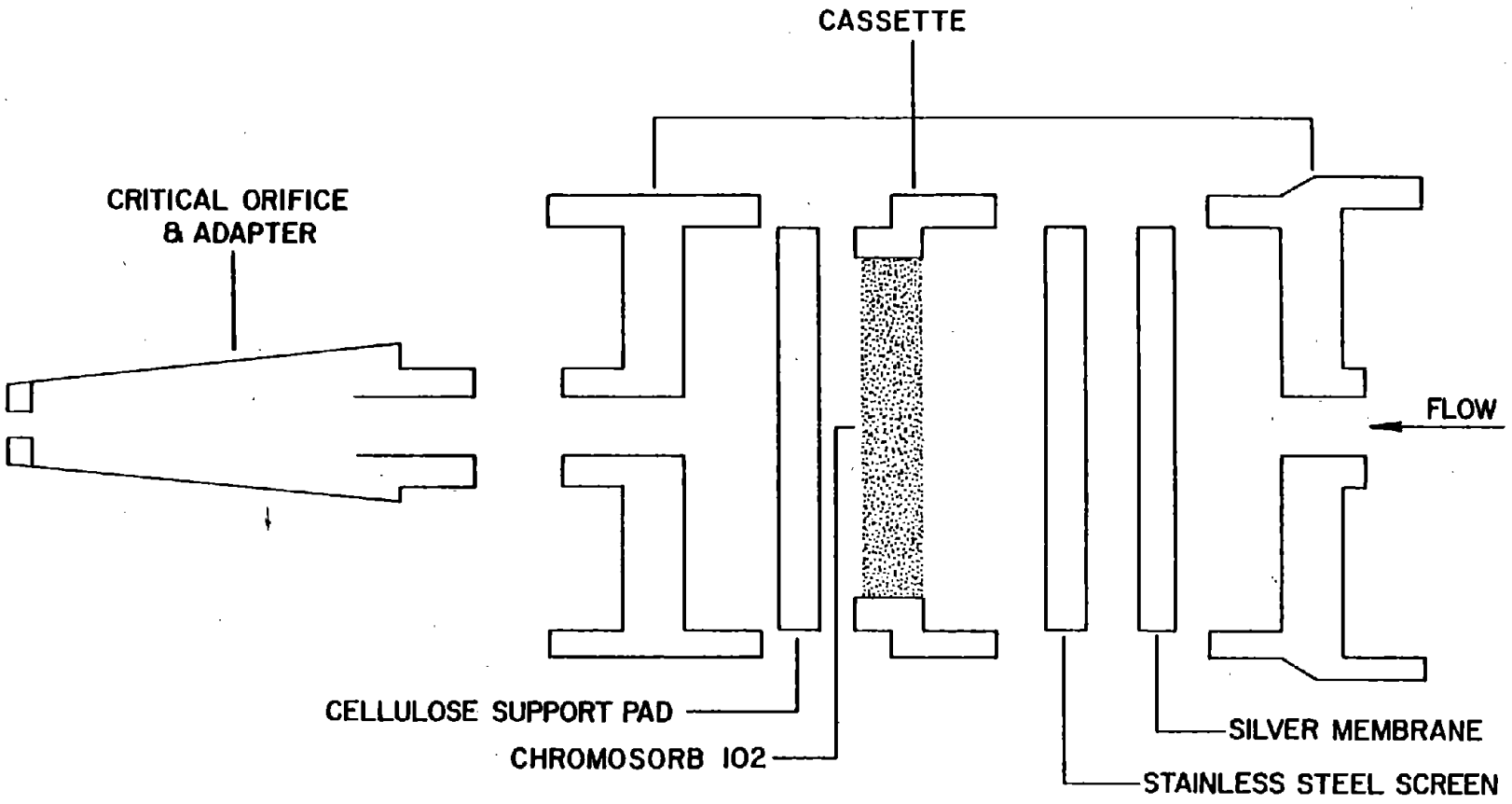

Figure 1. HIGH-VOLUME SAMPLING DEVICE FOR PNA

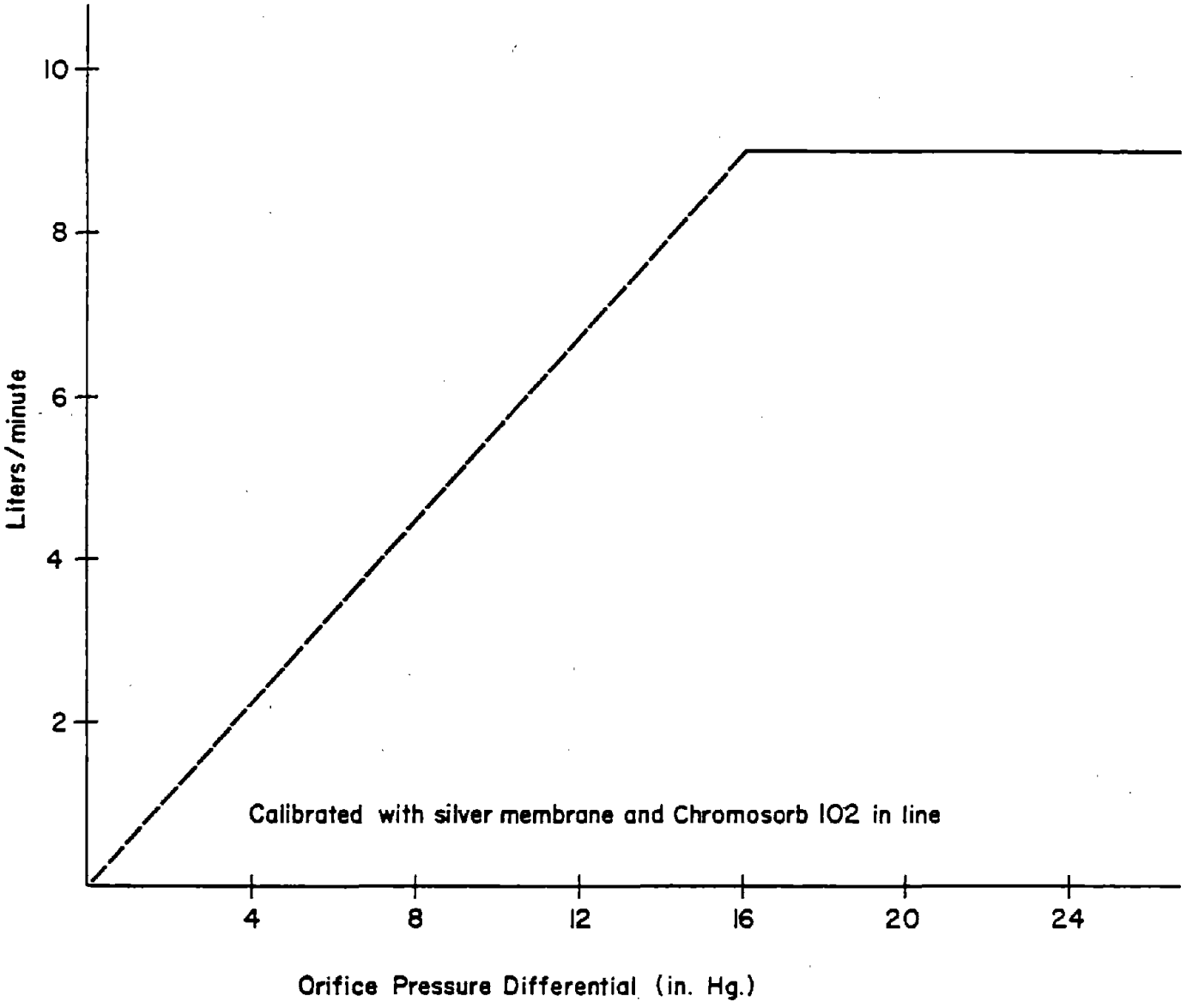

Figure 2. CALIBRATION CURVE FOR CRITICAL ORIFICE

sampling device shown in Figure 3 is used in conjunction with the high-flow pumps. This sampling device consists of a prewashed silver-membrane filter sandwiched between two methyl cellulose gaskets in a 37-mm cassette followed by 200 mg of Chromosorb 102 in 9 mm (inside diameter) glass tubing. The sampling train is calibrated at a flow rate of 2.0 liters/min with a soap-bubble-meter calibration train.

The sampling train for total particulates consists of a high-flow pump and a closed cassette containing a polyvinyl chloride (PVC) filter backed by a support pad. The sampling setup is calibrated at 2.0 liters/min with a soap-bubble-meter calibration train. The PVC filters are preweighed and sealed in the cassettes at SHL, using shrink bands to prevent contamination during storage and transport to the survey site. Preweighing is done at SHL for consistency of results and to eliminate laboratory bias.

The trace-metal sampling train consists of a high-flow pump and a 37-mm cassette containing a cellulose acetate filter backed by a support pad. The sampling train is calibrated at 2.0 liters/min. with a soap-bubble-meter calibration train. The cassettes are preassembled at Enviro with shrink bands to prevent contamination during storage and transport.

Sampling for respirable dust is conducted with a high-flow pump and a 37-mm cassette containing a PVC filter backed by a support pad. In this sampling train the cassette is preceded by a 0.5-inch miniature cyclone that removes the particulates in the nonrespirable range. The sampling train is calibrated at 1.7 liters/min with a soap-bubble-meter calibration train.

A calibration curve typical of the high-flow pumps used by Enviro is shown in Figure 4. All pumps are rechecked in the field on extended surveys and at the completion of the survey.

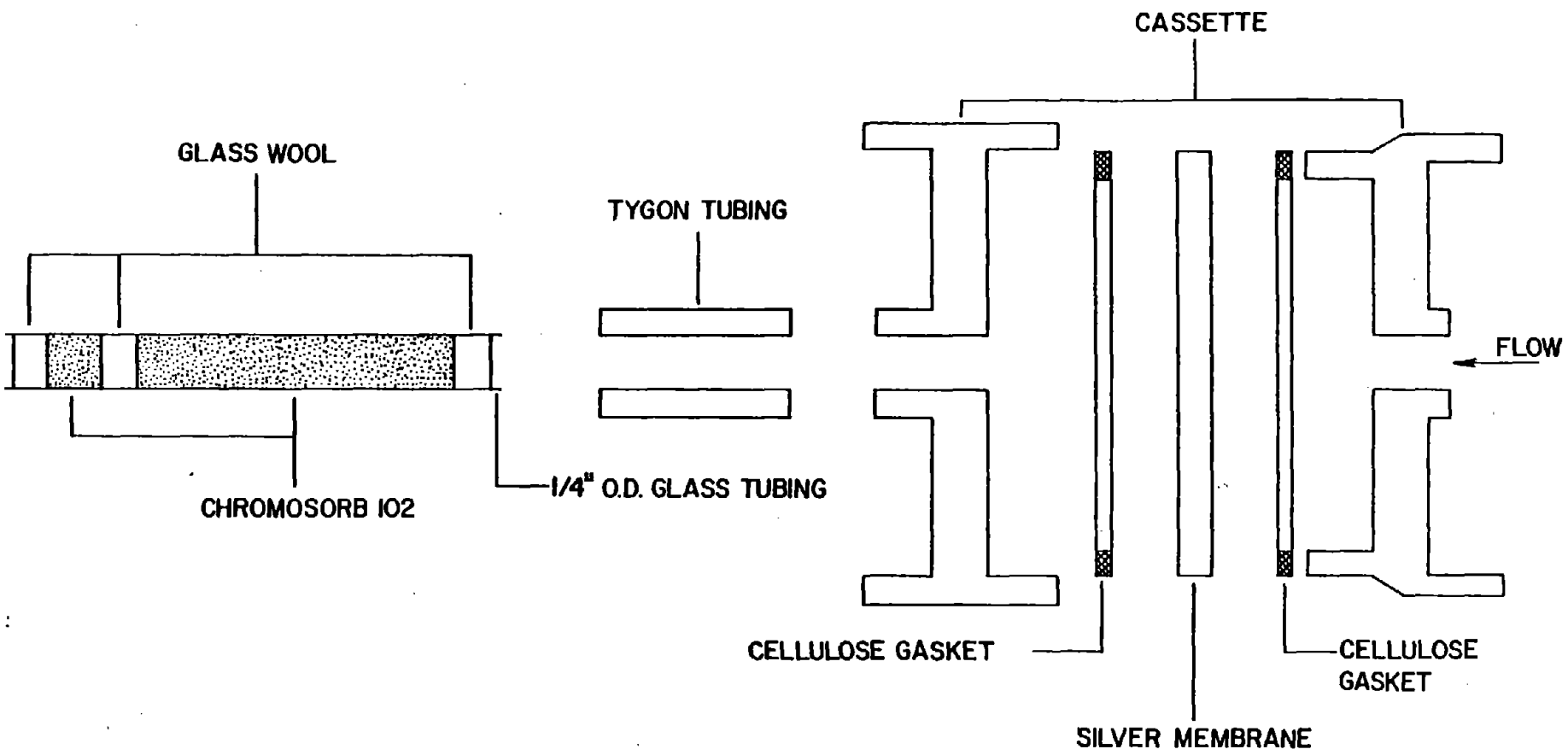

Figure 3. PERSONAL MONITORING DEVICE FOR PNA

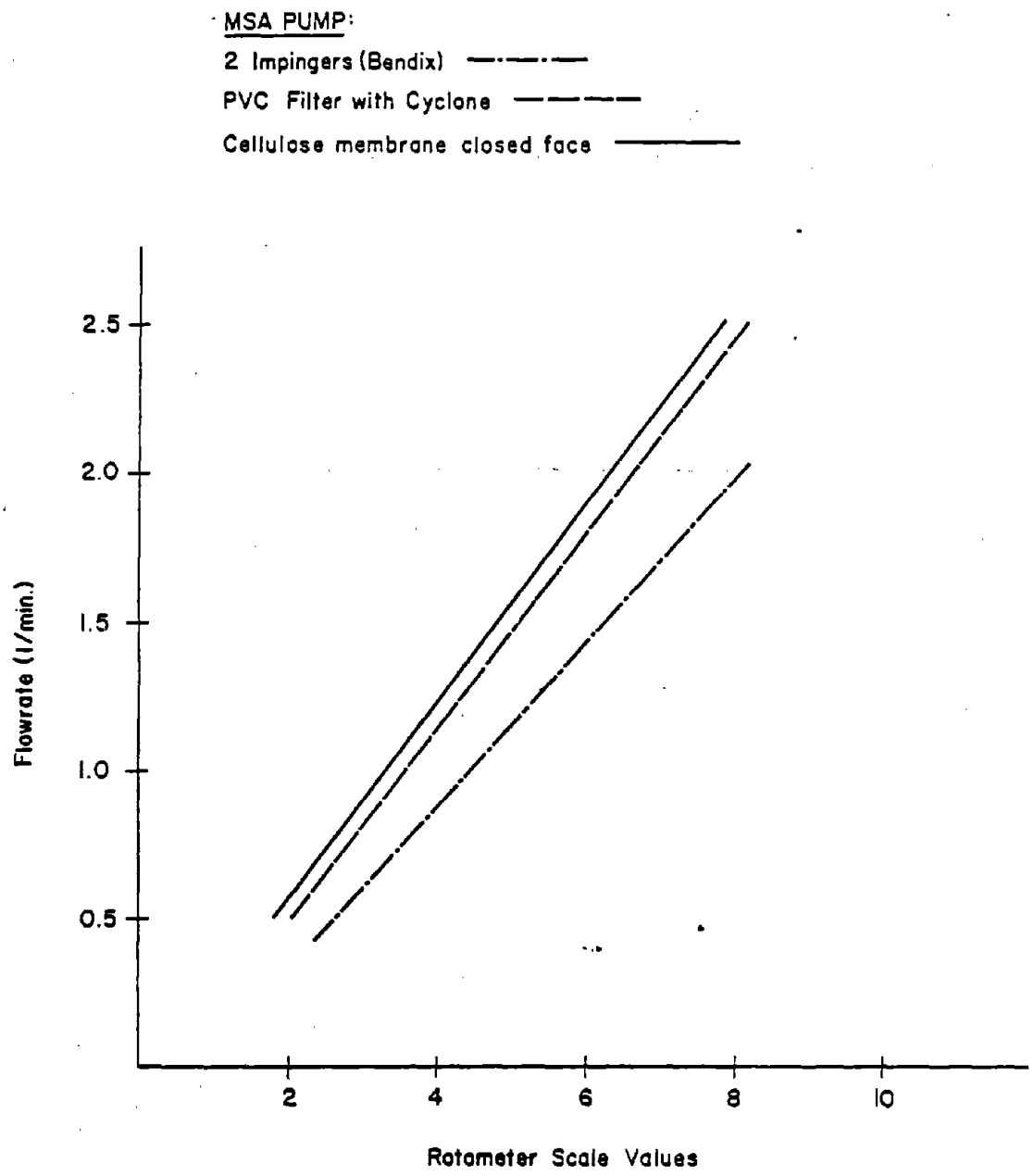

Figure 4. CALIBRATION CURVE FOR HIGH-FLOW PUMP

High-flow pumps calibrated at 2 liters/min and a 125-ml midget impinger containing 10% iodine in isopropyl alcohol will be used for sampling nickel carbonyl. The impinger is preceded by a Millipore filter (0.8 μ) to trap nickel particulates.

Low-flow pumps with either charcoal or silica-gel tubes are used in the collection of organics. Charcoal tubes (600 mg) are used in the collection of organic hydrocarbons. The sampling train of charcoal tube and sampling pump is calibrated at 100 ml/min with a soap-bubble-meter calibration train. The same calibrated setup at 100 ml/min is used for the sampling train of silica gel tube (875 mg) and sampling pump. This sampling train is used for collecting aromatic amines and alcohols.

To minimize breakage and contamination, charcoal tubes, silica-gel tubes, and other sampling media are transported to the survey site in their original sealed containers and are stored in these containers until they are used.

Direct-reading instruments are used for range-finding purposes to determine the types of compounds present and the order of magnitude of their amounts. For this reason these instruments will be used primarily during preliminary walk-through surveys. Instruments that are available include the HNU P101 analyzer for determining the levels of airborne hydrocarbons and the MSA carbon monoxide analyzer. Draeger detector tubes are used to check for toxic gases such as hydrogen sulfide, sulfur dioxide, ammonia, hydrogen cyanide, and mercaptans.

B. ONSITE PROCEDURE

Once a sampling site has been selected, the appropriate sampling train is assembled. For the high-volume area sampling of PNAs, air-driven pumps and preassembled cassettes (Figure 1) are used. These pumps are connected to convenient compressed-air outlets. All connections to plant outlets are made

with the approval and under the supervision of a plant representative as a safety precaution and to minimize disruption of plant operations. The preassembled cassette is wrapped in aluminum foil to minimize photodecomposition of the sample material. The high-volume sample cassette (Figure 1) is placed at breathing-zone height (about 5 to 6 feet above the surface). Sampling is conducted at a flow rate of 9.2 liters/min for an 8-hour period. Shorter sampling periods will be used in extremely dusty environments to prevent overloading of the cassette filters. The personal monitoring cassette wrapped in aluminum foil (Figure 3) is run at a flow rate of 1.5 liters/min for 8 hours.

PVC filters are used to collect samples for total particulates; and cellulose acetate filters are used for trace elements. Preweighed and sealed cassettes are used in sampling for total particulates; preassembled filter cassettes are used for trace elements. Air sampling is conducted at breathing-zone height with MSA high-flow pumps. Flow rates are 2 liters/min for both trace elements and total particulates.

C. RESPIRABLE DUST

For respirable-dust sampling, the cassette is preceded in the sampling train by a 0.5-inch miniature cyclone that removes particles in the nonrespirable size range. This setup is used for area and personal monitoring. Area sampling is conducted at breathing-zone height at a flow rate of 1.7 liters/min. An 8-hour sampling period is used, with shorter sampling times in dusty environments, to prevent overloading of the cassette.

D. ORGANICS

In sampling for organics, sampling trains with either charcoal tubes or silica-gel tubes and low-flow pumps calibrated at 100 ml/min are used. The sampling train is assembled as needed at the survey site to prevent contamination of the sampling media. This sampling-train setup is used for both area sampling and personal monitoring. Area sampling is conducted at about 5 to 6 feet above the surface to approximate the breathing-zone height.

Midget impingers (125 ml) and high-flow pumps calibrated at 2 liters/min will be used for long-term sampling of nickel carbonyl in plants where its formation is suspected. Area sampling is conducted at breathing-zone height.

Direct-reading instruments such as MSA or Draeger detector tube kits are used to check for toxic gases such as hydrogen sulfide, sulfur dioxide, carbon monoxide, nitrogen dioxide, hydrogen cyanide, ammonia, carbon disulfide, arsine, and mercaptans. An HNU P101 analyzer is used for measuring organics in the air. An MSA carbon monoxide analyzer is used to measure carbon monoxide levels in the plant.

During the sampling period, all sampling devices are checked on an hourly basis for

1. Overloading of the sampling media
2. Pump performance
3. Functioning of the sampling train

E. NOISE

All process areas are surveyed for noise. A sound-level meter (General Radio) is used in the walk-through survey to determine whether the sound level in any process area exceeds the OSHA 90-dBA 8-hour limit. In areas with a potential noise problem, a detailed noise survey is performed during the comprehensive survey, using the sound-level meter. The noise levels of sources within the problem area are mapped, and, where possible, isolines connecting points having the same noise level are indicated on the map. Noise dosimeters will be used where necessary to determine the weighted exposure for workers in these areas.

F. HEAT STRESS

Heat stress is measured by the wet bulb-globe temperature (WBGT) index. The WBGT index is determined during the comprehensive survey in the potentially hot environments previously identified in the walk-through survey.

G. RADIATION

Field checks for ionizing radiation using direct-reading instruments such as the Geiger-Mueller counter will not be made because radioactive contaminants, if present, would probably be in concentrations too low to be detected by these instruments. Instead, Enviro plans to collect bulk samples of coal or to conduct area sampling following the procedure for total particulates. These samples will be analyzed for low-level contamination.

H. IDENTIFICATION

At the start of the sampling period, each sample is identified by a sample number using the following representative labeling system:

1-AA-BBB-C-DD-EE-2-XX/YY/ZZ

where:

1	=	facility number
AA	=	code for agent to be analyzed
BBB	=	sequence number for sample
C	=	code for type of sample
DD	=	code for process area
EE	=	code for job classification
2	=	work shift
XX/YY/ZZ	=	date of collection

The sample numbers are logged in on sample data sheets (Figure 5) kept by the Enviro senior industrial hygienist. The sample data sheet contains detailed sampling information for each sample taken. The Enviro van is equipped to

INDUSTRIAL HYGIENE AND TOXICOLOGY

SAMPLE DATA SHEET

Sample No. _____ Analyze For _____ Date _____

Plant _____

Location Within Plant _____

Weather Conditions _____

____mmHg. _____ °F. _____ % R.H. Wind _____ MPH. Direction—W N E S W

Nature of Operation _____

Number of Employee's involved by Craft _____

Materials being used _____

Description of the Conditions of the Working Environment _____

Describe specific activities or operation covered by this sample _____

Sampling Data:

SAMPLING PERIOD		SAMPLE WEIGHT OR COUNT	SAMPLE VOLUME	CONCENTRATIONS			INSTRUMENT TYPE USED AND SERIAL NUMBER
TIME							
Start	Stop						
Total elapsed time				Sampling Rate			
Employee Monitored							

Comments _____

Requested Analysis _____

Figure 6. SAMPLE DATA SHEET

record wind-speed and wind-direction measurements, and additional equipment is available to record temperature and relative humidity. However, Enviro plans to use meteorological reports from nearby weather stations, when available, since these provide a more accurate reflection of variations in conditions.

I. SHIPPING

After sampling, samples are immediately sealed to prevent contamination or sample loss. Samples are stored in dry ice before shipping. Samples are then packed in "blue ice" in styrofoam containers specially designed for the shipment of materials under refrigeration. Filters, impinger liquids, charcoal and silica-gel tubes, and bulk samples are packed separately with styrofoam packing material to prevent breakage and contamination. This packaging system has been developed and used successfully in past projects.

All samples will be shipped to SHL, Iowa City, as soon as practical on completion of the sampling program. Samples will be handcarried to the analytical laboratory by an Enviro staff member if the plant site is near the laboratory or if the travel itinerary allows for a stopover in Iowa City. If this proves impractical, an overnight delivery service (e.g.), Federal Express or Emery Air Freight will be used.

III. ANALYTICAL METHODS

Section III.A. gives a general description of the various experimental requirements involved in the methods used in the analysis of samples for industrial hygiene studies of coal gasification and liquefaction pilot plants. Details of these analytical methods are provided in Sections III.B. through III.K.

A. GENERAL EXPERIMENTAL REQUIREMENTS

All analyses for the industrial hygiene characterization of coal gasification and liquefaction plants are performed by SHL. On receipt of the sample, analyses for PNAs and aza-PNAs are carried out in duplicate. The maximum permissible margin of error (percent variation) is $\pm$ 100%.

The two sections of charcoal tubes and silica-gel tubes are desorbed and analyzed individually, and then the results are totaled for each section. Each section is analyzed in triplicate even when no materials are found. The maximum percent variation found by SHL is 1 to 20%.

Instrumental calibrations are performed with pure standards. These calibrations are checked at least once a day for the mass spectrometer and once after every third sample for the gas chromatograph. For each PNA standard (see Table 1) a calibration factor is determined using three different concentrations. (For some of the PNA materials recommended for investigation, such as dibenzo(c,g)carbazole, no standards are available.) A known volume of each PNA sample is then analyzed. The resulting peaks of the individual PNA are measured and corrected using the calibration factor of the corresponding standard. Analysis of each PNA sample takes 1 to 2 days to complete.

Samples received are stored in the dark in a freezer at -10 C and are desorbed just before extraction.

TABLE 1
Commercial Suppliers of Standards

Standard	Supplier
Aromatic Alcohols	Polyscience
Aromatic amines	Aldrich, Fisher & Sigma
Aromatic hydrocarbons: benzene; toluene; xylene	Fisher
PNAs	
Anthracene	Aldrich
Phenanthrene	Aldrich
Fluorene	Pfaltz & Bauer
Pyrene	(*)
Fluoranthene	Aldrich
Acenaphthalene	Aldrich
Benz(a)anthracene	Pfaltz & Bauer
Benz(a)fluorene	ICN
Benz(b)fluorene	ICN
7,12-Dimethylbenz-(a)anthracene	Fisher/Sargent Welch
Dibenz(a,c)anthracene	ICN
Dibenz(a,h)anthracene	ICN
Perylene	Tridom
Naphthacene	Fisher/Sargent Welch
Benzo(e)pyrene	(*)
Benzo(a)pyrene	(*)
Dibenzo(a,h)pyrene	Pfaltz & Bauer
Dibenzo(a,i)pyrene	Sigma
Chrysene	Aldrich
Coronene	Aldrich
Triphenylene	Tridom
Anthanthrene	(*)
Aza-PNAs	
Dibenz(a,j)acridine	Sigma
Dibenzo(a,j)carbazole	Aldrich
Carbazole	Aldrich

* No information is available, sample available at SHL.

The desorption efficiencies (see Table 2) of the various adsorbents used for sampling (e.g., silica gel, charcoal, Chromosorb 102, and silver membrane) are determined by the following procedures:

1. A measured amount of the adsorbent is spiked with a known amount of the compound of interest dissolved in a suitable solvent, such as a mixture of methylene chloride and acetone. This compound may be a representative of the class of compounds being analyzed for, (Table 2). For example, the desorption efficiency for PNAs adsorbed on Chromosorb 102 is determined by using five homocyclic PNAs as representative of the PNA and aza-PNA class of compounds.

2. After the spiked adsorbent is permitted to dry (in the absence of external heat) and allowed to equilibrate at room temperature, it is subjected to the extraction procedure corresponding to the compound of interest, as outlined later in Section III.B. through III.E. and III.G. through III.J.

3. Without prepurification and fractionation, the compound of interest is then analyzed by the method detailed in Sections III.B. through III.E. and III.G. through III.J. From the amount recovered, the percentage desorption efficiency is calculated for each adsorbent with respect to the compound or class of compounds of interest.

TABLE 2
Desorption Efficiencies of Various Adsorbents

Adsorbent	Class of Compounds	Representative Compound Used	Desorption Efficiency (%)
Silica gel	Aromatic amines	Aniline	98
		N,N-Dimethylaniline	100
		o-Anisidine	100
		p-Anisidine	100
Silica gel	Phenols	Phenol	100
		Cresol	100
Charcoal	Hydrocarbon vapors	Benzene	98
		Toluene	95
		Xylene	93
Chromosorb 102	PNAs and aza-PNAs	Five unspecified standards	Proprietary information
Silver membrane	PNAs and aza-PNAs	None performed	None

For the gas chromatography(GC) analyses, a Varian Model 2700 or 3700 gas matograph with dual-column flame-ionization detectors (FID) is used. The instrument is equipped with auto-integrator model CDS-111.

The mass spectrometer (MS) is a Finnigan System model 4023 that includes the 2300 NCOS data system. Parameters for the calibration of the MS are as follows:

Calibration standard:	perfluorotributylamine (FC_43)
Calibration range:	low mass, 69; high mass, 614
Mass-spectrum stability:	$\pm$0.05 atomic mass unit (amu) or better over an 8-hour period

Masses are assigned by the computer from 69 to 614 using a least-squares analysis to an error of less than 150 millimass units (mmu's). (i.e., a resolution within $\pm$0.05 mass unit can be obtained.)

The perfluorotributylamine is a calibration gas provided with this broad-range MS system to optimize its resolution capabilities and to indicate whether the instrument is resolving properly.

For high-pressure liquid chromatography (HPLC) a Waters Associates Model 240ALC fluorescence-type detector is used. The source of the excitation light (254 nm) is a deuterium discharge tube. The detector is of the fixed-wavelength type and uses a 420E filter. It is sensitive to light of wavelength greater than 425 nm.

B. ANALYSIS OF AROMATIC AMINES IN AIR SAMPLES

Silica-gel tube analysis of aromatic amines is performed for the following analytes:

Aniline
N,N-Dimethylaniline
p-Anisidine
o-Anisidine

NIOSH validated Physical and Chemical Analysis method (P & CAM) 168 (1) is used (see Appendix B for details) with the following modifications:

1. Desorption with 95% aqueous ethyl alcohol*
2. Conditions for GC columnn I (used for confirmation analysis):
   a. 6 ft x 0.25 in. i.d. glass column packed with 10% Carbowax 20 M/2% KOH on 80/100 mesh Chromosorb W (AW)
   b. Column temperature: 150 C held isothermally for 2 min, programmed at 10 C per min to 200 C
   c. Injector temperature: 265 C
   d. Detector temperature: 265 C
   e. Air flow rate: 30 ml/min
   f. Hydrogen flow rate: 350 ml/min
   g. Carrier-gas (helium) flow rate: 48 ml/min (30 psi)
   h. Attenuation: 12 x 16

*Acetone is the desorption solvent described in NIOSH method P & CAM 168. It reacts with aromatic amines to produce Schiff bases and has therefore been replaced here with ethyl alcohol.

3. Conditions for GC column II (used for identification and quantitation)
   a. 10 ft x 0.125 in. i.d. stainless-steel column packed with 10% FFAP on 80/100 mesh Chromosorb W (acid washed/dimethyl-chlorosilane)
   b. Column temperature: 180 C (isothermal)
   c. Injector temperature: 250 C
   d. Detector temperature: 250 C
   e. Air flow rate: 30 ml/min
   f. Hydrogen flow rate: 350 ml/min
   g. Carrier-gas (helium) pressure: 40 psi

Should it be necessary to analyze for naphthylamines, Column II will be used under the conditions described above.

All retention times of the above-mentioned aromatic amines will be measured with reference to the solvent front (ethyl alcohol).

Detection limits (assuming a 20-liter air sample) are listed below:

Compound	Detection Limit (ppm)
Aniline	0.15
N,N-Dimethylaniline	0.05
o-Anisidine	0.05
p-Anisidine	0.20

C. ANALYSIS OF AROMATIC ALCOHOLS IN AIR SAMPLES

Silica-gel tube analysis of aromatic alcohols is performed for the following analytes:

Phenol
Cresols (isomers)
o-Ethyl phenol
p-Ethyl phenol
2,3-Xylenol
3,5-Xylenol

NIOSH validated method S167 for cresols (1) is used (see Appendix B for details) with the following modifications:

1. Desorption with 95% aqueous ethyl alcohol
2. GC conditions: as described for GC columns I and II in Section III.B. for the analysis of aromatic amines in air samples

All retention times of the above aromatic alcohols are measured with reference to the solvent front (ethyl alcohol).

Detection limits (assuming a 20-liter air sample) are listed below:

Compound	Detection Limit (ppm)
p-Ethyl phenol	1.0
o-Ethyl phenol	1.0
2,3-Xylenol	1.0
3,5-Xylenol	1.0

D. ANALYSIS OF SELECTED ORGANIC (HYDROCARBON) VAPORS IN AIR SAMPLES

Charcoal-tube analysis for organic hydrocarbon solvents was performed for the following analytes:

Benzene
Toluene
Xylene

NIOSH validated method P & CAM 127 (1) is used (see Appendix B for details) with the following modifications:

1. GC column is a 10 ft x 0.125 in. i.d. stainless-steel column packed with 10% FFAP on 80/100 mesh Chromosorb W (acid washed/dimethyl-chlorosilane)
2. Column temperature: 80 C (isothermal)
3. Injector temperature: 200 C
4. Detector temperature: 200 C
5. Air flow rate: 350 ml/min
6. Hydrogen flow rate: 35 ml/min
7. Carrier-gas (helium) flow rate: 94 ml/min (55 psi)
8. Attenuation: 12 x 32

Retention times of the above hydrocarbon solvents are measured with reference to the solvent front (carbon disulfide). Detection limits (assuming a 20-liter air sample) are found to be 30 to 40 ng for the above-listed hydrocarbons.

E. ANALYSIS OF TOTAL PARTICULATE MATTER IN AIR SAMPLES

Total-particulate samples on PVC filters are determined gravimetrically from the difference in the weights of the PVC filters before and after air sampling. Values for total particulates are expressed in weight per cubic meter of air samples.

Optical sizing is performed on respirable dust samples collected on PVC filters. For sizing, the particulate sample is prepared for optical microscopy by rendering the PVC filter transparent with an immersion fluid. The prepared slide is focused in the field of the optical microscope and particles are sized using a reticular grid of known dimensions. The most commonly used grid is the Porton reticle, which is mounted in the ocular lens so that the grid is superimposed on the field of the microscope. The reticle is calibrated at the magnification to be used by means of a stage micrometer. Only one reading in the field of the grid is required for sizing with the Porton reticle.

F. ANALYSIS OF "BENZENE-SOLUBLE" COMPOUNDS IN AIR SAMPLES

The total "benzene-soluble" compounds collected on silver-membrane sampling filter include, among other organic chemicals, all those PNA compounds listed in Table 1. NIOSH validated method P & CAM 217 (1) is used (see Appendix B for details), except that the extraction is performed ultrasonically with cyclohexane instead of benzene. (This substitution of solvents is necessary because of benzene's potential health hazards.)

After extraction, the cyclohexane solution is filtered through a prewashed plug of glass wool and concentrated to a 10-ml volume in a Kuderna-Danish (K-D) concentrator. A sample is then analyzed to determine approximately the total amount of "benzene-soluble" compounds present. If sufficient amounts of "benzene-soluble" compounds are evident, the 10-ml sample is divided into two 5-ml portions, and each portion is individually analyzed on a GC-MS/HPLC combination and/or by a capillary GC technique (8).

G. ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBONS (PNA) IN AIR SAMPLES

1. Principle:

Airborne particulate samples, containing PNAs and their aza-analogs, are collected on two-stage samplers consisting of a silver-membrane filter with a Chromosorb 102 adsorbent backup.

The silver-membrane filter is ultrasonically extracted according to NIOSH validated method P & CAM 217 (1) (see Appendix B for details). The Chromosorb 102 adsorbent is Soxhlet-extracted with a 1:1 methylene chloride-methanol mixture.

Extracts of both adsorbent and filter are then subjected to prepurification and fractionation when necessary, using HPLC and a μ-Bondapak NH_2 column. The fractions containing PNAs are then concentrated and injected into a GC-MS/HPLC system. Each GC peak pertaining to the PNAs listed in Table 1 is identified from its mass spectrum, and its retention time, as compared with the PNA reference compounds.

2. Breakthrough

Enviro has conducted studies of breakthrough and recovery on both area and personal air-sampling devices designed for the collection of PNAs with a dynamic U-tube system (2, 3). Of particular interest in these preliminary studies is the relative capability of each sampling device to effectively capture low-molecular-weight polynuclear aromatic compounds, thus insuring against losses due to breakthrough for a field concentration over a standard 8-hour sampling period. In initial qualitative testing, undertaken to establish confidence limits for breakthrough, acenaphthene was used as an appropriate low-molecular-weight PNA.

In breakthrough studies for the high-volume area sampler (containing approximately 2.75 grams of Chromosorb 102), 20-mg quantities of acenaphthene typically were injected into the U-tube flow chamber; the volume of air sampled was 2000 liters, and the sampling period was generally 4 hours. For the personal sampler (containing 200 mg of Chromosorb 102), 0.5-mg quantities were injected into the U-tube system; air sample volumes were on the order of 360 liters for a 4-hour sampling period.

The results obtained indicated that there was no breakthrough for either device under the test conditions described; sample recovery was essentially 100%. Based on the results obtained in these preliminary tests for area samplers and personal samplers, there is little reason to anticipate PNA breakthrough in less than 8 hours for the area sampler at air concentrations below 5 mg/m^3 and for the personal sampler below 0.75 mg/m^3.

In terms of typical results obtained in rangefinding for concentrations of cyclohexane-soluble material in air for coal gasification and liquefaction processes (Table 3), both devices insure substantially against breakthrough losses of PNAs likely to be found in the work environment -- by many orders of magnitude at the lower limit.

TABLE 3
Cyclohexane-Soluble Material for a Coal
Liquefaction Plant

Sample	Sample Volume (liters)	Silver Membrane Weight increase	mg/m^3
1	4316	0.079	0.02
2	2318	0.125	0.05
3	3597	0.014	0.01
4	4316	0.263	0.06
5	4316	0.088	0.02

3. Experimental

a. Isolation

The silver-membrane stainless-steel screen is ultrasonically extracted with cyclohexane according to NIOSH validated method P & CAM 217 (1). (The use of benzene as the extracting solvent is avoided because it presents a health hazard.) The Chromosorb 102 adsorbent is extracted in a Soxhlet for 12 hours using 150 ml of a 1:1 methylene chloride-methanol mixture (4). (The use of methylene chloride alone is found to be unsatisfactory for the complete extraction of all polar constituents.) During both extractions, the solutions are protected from light by wrapping each apparatus with foil.

Each extract is transferred quantitatively to a Kuderna-Danish sample concentrator after filtration through a prewashed plug of glass wool. Both the Chromosorb filter and the silver membrane are washed again with the extraction solvent and added to the individual extracts. These extracts are then further processed, individually in the case of samples collected in a walk-through plant visit, or after being combined together in the case of samples taken in a comprehensive plant visit. In either case, further processing entails first evaporating the individual or combined extract(s) on a steam bath down to approximately 10 ml. Approximately 5 ml of this concentrate is rinsed out with two 5-ml portions of the appropriate solvent and divided equally between the two tubes, in order to provide a spare sample if the other sample is lost. Each tube is then wrapped in foil and stored in a freezer until analysis. Desorption efficiencies for both filters are found to be approximately 100%.

b. Prepurification and Fractionation

The PNAs are separated from aliphatic hydrocarbons and polar compounds by an HPLC technique (5), (provided the latter compounds are present).

Portions of the extracts described in section (a) above are concentrated to approximately 1 ml and injected into a 30 cm x 4 mm i.d. μ-Bondapak NH_2 column. The PNAs are eluted with n-hexane. The μ-Bondapak detection limits for each PNA determined by this method are listed in Table 4, which gives the detection limit for the capillary GC method for comparison.

All the PNA and aza-PNA compounds listed in Table 4 are satisfactorily resolved by the GC-MS system using mixtures of pure PNA's, except for chrysene, triphenylene, and benz(a)anthracene as one group and benz(a)pyrene and benz(e)-pyrene as another group. These five PNA compounds are, however, successfully resolved and quantitated by HPLC (6), fitted with a fluorescence detector (7).

The use of μ-Bondapak NH_2 provides a separation of PNAs that depends on the number of condensed rings (5). Each of the fractions is then analyzed by GC-MS, as outlined below.

c. Analysis

The method described below in section (i) uses a GC-MS/HPLC system for the analysis of PNA samples. However, as an alternative to this technique, the capillary-GC method, described later in section (ii) is also being developed and will be used if it proves to be more rapid, cost effective, and as sensitive.

TABLE 4

Detection Limits of the GC-MS and Capillary GC Techniques

Compound	Detection Limits (nanograms) GC-MS	Capillary GC
Anthracene	1.0	1.0
Phenanthrene	1.0	0.8
Fluorene	1.0	0.8
Pyrene	1.0	1.3
Fluoranthene	1.0	2.0
Acenaphthalene	1.0	0.5
Benz(a)anthracene	2.0	3.0
Benz(a)fluorene	4.0	2.0
Benz(b)fluorene	4.0	2.0
7,12-Dimethylbenz(a)anthracene	7.0	3.0
Dibenz(a,c)anthracene	4.0	5.0
Dibenz(a,h)anthracene	4.0	5.0
Perylene	4.0	2.0
Naphthacene	9.0	8.0
Benzo(e)pyrene	5.0	3.0
Benzo(a)pyrene	6.0	3.0
Dibenzo(a,h)pyrene	4.0	10.0
Dibenzo(a,i)pyrene	4.0	10.0
Chrysene	4.0	3.0
Coronene	5.0	8.0
Triphenylene	2.0	3.0
Anthanthrene	44.0	5.0
Indo(1,2,3-cd)pyrene	17.0	5.0
Aza-PNA		
Dibenz(a,j)acridine	4.0	-
Dibenzo(a,j)carbazole	4.0	-
Carbazole	2.0	5.0

(i) GC-MS/HPLC System. The GC-MS parameters adopted for the separations and quantitation, using the PNA reference samples listed in Table 1, are as follows:

1. GC column (8): 6 ft x 0.079 in i.d. glass column packed with 3% OV-17 on 80/100 mesh Supelcoport (purchased from Supelco Inc.)
2. Column temperature: 8 C min to 260 C, then held at 260 C for 50 min
3. Injector temperature: 240 C
4. GC-MS interface temperature: 325 C
5. Carrier-gas (helium) flow rate: 30 ml/min
6. MS ionizer block temperature: 250 C
7. MS electron multiplier voltage: 1800 V
8. MS electron energy: 70 eV
9. MS emission current: 500 mA

All GC analyses of the referenced PNA compounds produce symmetrical gaussian peaks, each of which is identified by the MS. The retention time of each of the PNAs listed in Table 1 is measured with reference to the solvent front. The PNA that elutes last is coronene (approximately 74 min).

The HPLC parameters adopted for this separation are as follows:

1. Column: Two C_{18} μ-Bondapak reverse-phase columns, 30 cm x 3.9 mm, attached in series
2. Solvent: 70:30 acetonitrile-water mixture run isocratically
3. Flow rate: 2.5 ml/min

Fluoranthene is used as an internal standard, with an arbitrary retention index (RI) of 1.00 (actual retention time is 10 min). These RI values for the five PNA compounds unresolved by the GC-MS method are provided in Table 5, which also includes the detection limit for each compound.

TABLE 5

HPLC Retention Indices and Detection Limits

for PNAs Not Resolved by GC-MS

PNA	RI Value	Detection Limit (nanograms)
Benz(a)anthracene	1.375	1.0
Chrysene	1.335	6.0
Triphenylene	1.243	18.0
Benz(a)pyrene	1.912	1.0
Benz(e)pyrene	1.750	13.0

(ii) GC-Capillary Method. This method is according to that described by Lee, Vessilaras, and White (9) which is shown to be reproducible. The GC parameters used are as follows:

1.	GC equipment:	Varian Model 3700 equipped with an autointegrator and a dual flame-ionization detector
2.	GC column:	15 m x 0.2495 mm i.d. glass capillary column packed with a 0.34-micrometer film thickness of SE-52 (from J & W Scientific)
3.	Column temperature:	50 C to 250 C at 2 C/min
4.	Injector temperature:	300 C
5.	Detector temperature:	320 C
6.	Carrier-gas (helium) pressure:	20 psi

Retention indices for a number of PNA compounds, including those listed previously, are calculated from the following Van Der Dool and Kratz equation (10), based on comparison with four PNA internal standards (naphthalene, phenanthrene, chrysene, and dibenzanthracene) (11):

$$I = 100n + \left[\frac{X - M_n}{M_{n+1} - M_n}\right]$$

where:

I = retention index of the PNA compound of interest
X = measured retention time of the PNA of interest
M = measured retention time of any aromatic compound
n = number of rings in standard compound eluting immediately ahead of X (where only four standard compounds are used)
n + 1 = number of rings in standard compound eluting immediately after X

The defined RI values for the bracketing standards are listed below:

Standard	Defined RI Value
Naphthalene	200
Phenanthrene	300
Chrysene	400
Dibenzanthracene	500

Relative to these standards, Table 6 lists typical examples of calculated RI values for PNA compounds. The calculated values were shown to be in very good agreement with reported values (9).

By this technique, all PNA compounds listed in Table 1 have been adequately resolved, have been identified from their RI values, and can be satisfactorily quantitated. Detection limits are listed in Table 4.

H. ANALYSIS FOR AIRBORNE TOXIC GASES

1. Nickel Carbonyl:

Since there is no effective detector tube currently on the market for the analysis of nickel carbonyl, an alternative method will be used. Alternative nonchemical detection methods include Fourier transform infrared absorption spectroscopy (FTIR), plasma chromatography, and chemiluminescent techniques. However, a more rapid and equally sensitive technique is the chemical method (12). In this technique impinger samples of nickel carbonyl are analyzed colorimetrically as follows:

> An air sample containing nickel carbonyl is bubbled through an alcoholic iodine solution. The entire bubbler solution is evaporated and dissolved in dilute acid; this solution is then neutralized and α-furildioxime is added to form a chloroform-extractable nickel complex. The absorbance at 425 nm is determined and compared to the absorbance of standards.

TABLE 6

Calculated RI Values for PNA Compounds

PNA Compound	Found by SHL	Reported (9)
2-Methylnaphthalene	218.14 ± 0.28	217.80 ± 0.13
Acenaphthalene	244.63 ± 0.15	244.63 ± 0.19
Fluorene	268.25 ± 0.16	268.17 ± 0.15
Anthracene	301.72 ± 0.26	301.69 ± 0.08
Fluoranthene	344.53 ± 0.28	344.01 ± 0.16
Pyrene	351.43 ± 0.30	351.22 ± 0.08
Benz(a)anthracene	398.72 ± 0.20	398.05 ± 0.08

The detection limit of nickel carbonyl by this method ranges from less than parts per billion to parts per million.

2. Other Gases:

Other airborne toxic gases include the following:

Hydrogen sulfide
Carbon monoxide
Carbon dioxide
Hydrogen cyanide
Ammonia
Carbon disulfide
Thiophene
Arsine

Wherever possible, the above gases are analyzed at the site with detector tubes. Compared with analysis involving impinger sampling technique, this method is considered to be quite rapid, sufficiently sensitive, and simple to apply both for qualitative as well as for quantitative, shortand long-term analysis.

I. ANALYSIS FOR AIRBORNE TRACE METALS

Trace metals to be analyzed include the following:

Arsenic
Cadmium
Beryllium
Nickel
Tellurium
Mercury
Copper
Manganese
Strontium
Magnesium

Analyses of these metals are performed by the atomic absorption procedure described in NIOSH method P & CAM 173 (1) (see Appendix B for details).

J. ANALYSIS FOR AIRBORNE METHYL THIOPHENE

NIOSH-validated method P & CAM 255 (1) will be followed (see Appendix B for details).

K. ANALYSIS FOR AIRBORNE MERCAPTANS

A detector tube is used at the site for this analysis. The reason for using this method of analysis is given in Section III.H.2.

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APPENDIX A

METHODS ATTEMPTED BUT FOUND INEFFECTIVE FOR THE ANALYSIS OF PNAs IN AIR SAMPLES

APPENDIX A

METHODS ATTEMPTED BUT FOUND INEFFECTIVE FOR THE ANALYSIS OF PNAs IN AIR SAMPLES

The following methods of analysis were attempted at the Iowa State Hygienic Laboratory, Iowa City, but they were found to be ineffective for the analysis of PNAs in air samples.

GC-MS With Dexsil 300 Stationary Phase (1)

The GC-MS analysis of a PNA mixture reported by Lao et al. (1) could not be reproduced. The GC parameters used for the fractionation and quantitation of the PNA reference compounds were as follows:

1. Column: 12 ft x 0.125 in. i.d. stainless-steel column packed with 6% Dexsil 300 on 80/100 mesh Chromosorb W (HP) (purchased from Applied Science)
2. Sample injector temperature: 325 C
3. GC-MS interface temperature: 325 C
4. Carrier-gas (helium) flow rate: 40 ml/min
5. Initial temperature: 165 C held for 2 min
6. Programmed temperature: 4 C /min to 295 C
7. Final temperature: 295 C held for 50 min

Problems encountered include excessive bleeding of the 6% Dexsil 300 column, even after conditioning it for 6 days at 375 C. Such bleeding completely masks peaks having retention times greater than triphenylene (retention time 29 min). Anomalous peaks showed on the MS, which are due to breakdown products from the GC injection port septum at the operational injector temperature of 325 C, thus further masking high retention peaks. Septa of various materials, including silicone, were used, but all gave unsuccessful results.

GC-MS With Nematic Liquid-Crystal Stationary Phase (2)

Separation of the reference PNA hydrocarbons can also be accomplished by using a GC column packed with a pneumatic liquid-crystal stationary phase: N,N'bis-(p-phenylbenzylidine)α,α'-bis-(p-toluidine)(2). The GC parameters used were as follows:

1. Column: 6 ft x 0.079 in i.d. glass column packed with 1.5% SP-301 on 100/120 mesh Supelcoport (column prepared at SHL; packing purchased from Supelco, Inc.)
2. Column temperature: 270 C
3. Injector temperature: 260 C
4. Detector temperature: 270 C
5. Carrier gas (nitrogen) flow rate: 20 ml/min

The GC analysis of the PNA reference samples was accomplished; however, the earlier lack of adequate sensitivity makes this method less desirable than that with OV-17 described in Section III.G.3.C(i). Examples of the minimum detection limits of selected PNAs are listed below:

PNA	Detection Limit (ng)
Triphenylene	40
Chrysene	40
Benzo(a)pyrene	50
Benzo(e)pyrene	30

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APPENDIX B

NIOSH ANALYTICAL METHODS

ORGANIC SOLVENTS IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Organic Solvents (See Table 1)	Method No:	P&CAM 127
Matrix:	Air	Range:	For the specific compound, refer to Tables I&II
Procedure:	Adsorption on charcoal desorption with carbon disulfide, GC		
Date Issued:	9/15/72	Precision:	10.5% RSD
Date Revised:	7/15/74	Classification:	See Table 1

1. Principle of the Method

   1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

   1.2 The charcoal in the tube is transferred to a small, graduated test tube and desorbed with carbon disulfide.

   1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

   1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

   The lower limit in mg/sample for the specific compound at 16 x 1 attenuation on a gas chromatograph fitted with a 10:1 splitter is shown in Table 1. This value can be lowered by reducing the attenuation or by eliminating the 10:1 splitter.

3. Interferences

   3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

   3.2 When two or more solvents are known or suspected to be present in the air, such information including their suspected identities, should be transmitted with the sample; since with differences in polarity, one may displace another from the charcoal.

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Hence, retention time data on a single column, or even on a number of columns, cannot be considered as proof of chemical identity. For this reason it is important that a sample of the bulk solvent(s) be submitted at the same time so that identity(ies) can be established by other means.

3.4 If the possibility of interference exists, separation conditions (column packing, temperatures, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The mean relative standard deviation of the analytical method is 8%. (Ref. 11.4).

4.2 The mean relative standard deviation of the analytical method plus field sampling using an approved personal sampling pump is 10% (Ref. 11.4). Part of the error associated with the method is related to uncertainties in the sample volume collected. If a more powerful vacuum pump with associated gas-volume integrating equipment is used, sampling precision can be improved.

4.3 The accuracy of the overall sampling and analytical method is 10% (NIOSH's unpublished data) when the personal sampling pump is calibrated with a charcoal tube in the line.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more solvents suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists. During sample storage the more volatile compounds will migrate throughout the tube until equilibrium is reached (33% of the sample on the backup section).

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 An approved and calibrated personal-sampling pump for personal samples. For an area sample any vacuum pump whose flow can be determined accurately at 1 liter per minute or less.

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in frontof the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 ℓpm.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (20 ft x 1/8 in) with 10% FFAP stationary phase on 80/100 mesh, acid-washed DMCS Chromosorb W solid support. Other columns capable of performing the required separations may be used.

6.5 A mechanical or electronic integrator or a recorder and some method for determining peak area.

6.6 Glass stoppered micro tubes. The 2.5-mℓ graduated microcentrifuge tubes are recommended.

6.7 Hamilton syringes: 10 µl, and convenient sizes for making standards.

6.8 Pipets: 0.5 mℓ delivery pipets or 1.0 mℓ type graduated in 0.1 mℓ increments.

6.9 Volumetric flasks: 10 mℓ or convenient sizes for making standard solutions.

7. Reagents

7.1 Spectroquality carbon disulfide (Matheson Coleman and Bell)

7.2 Sample of the specific compound under study, preferably chromatoquality grade.

7.3 Bureau of Mines Grade A helium.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, the ends of the tube should be broken to provide an opening at least one-half the internal diameter of the tube (2mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be vertical during sampling.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 The flow, time, and/or volume must be measured as accurately as possible. The sample should be taken at a flow rate of 1 ℓpm or less to attain the total sample volume required. The minimum and maximum sample volumes that should be collected for each solvent are shown in Table 1. The minimum volume quoted must be collected if the desired sensitivity is to be achieved.

8.3.6 The temperature and pressure of the atmosphere being sampled should be measured and recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly before they are shipped to minimize tube breakage during shipping.

8.3.10 Samples of the suspected solvent(s) should be submitted to the laboratory in containers furnished by NIOSH for such purpose. These liquid bulk samples should not be transported in the same container as the samples or blank tube. If possible, a bulk air sample (at least 50ℓ air drawn through tube) should be shipped for qualitative identification purposes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In prepration for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a small stoppered test tube. The separating section of foam is removed and discarded; the second section is transferred to another test tube. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, one-half ml of carbon disulfide is pipetted into each test tube. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period. The use of graduated glass-stoppered, microcentrifuge tubes is recommended so that one can observe any apparent change in volume during the desorption process. Carbon disulfide is a very volatile solvent, so volume changes can occur during the desorption process depending on the surrounding temperature. The initial volume occupied by the charcoal plus the 0.5 mℓ CS_2 should be noted and corresponding volume adjustments should be made whenever necessary just before GC analysis.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 85 cc/min. (70 psig) helium carrier gas flow.
2. 65 cc/min. (24 psig) hydrogen gas flow to detector.
3. 500 cc/min. (50 psig) air flow to detector.
4. 200°C injector temperature.

5. 200°C manifold temperature (detector)
6. Isothermal oven or column temperature - refer to Table 1 for specific compounds.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blowback or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10 µℓ syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µℓ to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µℓ aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back a short distance to minimize evaporation of the sample from the tip of the needle. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process for a given compound, provided the same batch of charcoal is used. The Physical and Chemical Analysis Branch of NIOSH has found that the desorption efficiencies for the compounds in Table 1 are between 81% and 100% and vary with each batch of charcoal.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 5cm, 4-mm I.D. glass tube, flame-sealed at one end (similar to commercially available culture tubes). This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped

with Parafilm. A known amount of the compound is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. The amount injected is usually equivalent to that present in a 10-liter sample at a concentration equal to the federal standard.

At least five tubes are prepared in this manner and allowed to stand for at least overnight to assure complete abosrption of the specific compound onto the charcoal. These five tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.3.

Two or three standards are prepared by injecting the same volume of compound into 0.5 mℓ of CS_2 with the same syringe used in the preparation of the sample. These are analyzed with the samples.

The desorption efficiency equals the difference between the average peak area of the samples and the peak area of the blank divided by the average peak area of the standards, or

$$\text{desorption efficiency} = \frac{\text{Area sample} - \text{Area blank}}{\text{Area standard}}$$

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 mℓ CS_2 because samples are desorbed in this amount of CS_2. To minimize error due to the volatility of carbon disulfide, one can inject 20 times the weight into 10 mℓ of CS_2. For example, to prepare a 0.3 mg/0.5 mℓ standard, one would inject 6.0 mg into exactly 10 mℓ of CS_2 in a glass-stoppered flask. The density of the specific compound is used to convert 6.0 mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5mℓ versus peak area.

NOTE: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 The weight, in mg, corresponding to each peak area is read from the standard curve for the particular compound. No volume corrections are needed, because the standard curve is based on mg/0.5 mℓ CS_2 and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{Correct mg} = mg_s - mg_b$$

where:

mg_s = mg found in front section of sample tube

mg_b = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 The corrected amounts present in the front and backup sections of the same sample tube are added to determine the total measured amount in the sample.

10.4 This total weight is divided by the determined desorption efficiency to obtain the total mg per sample.

10.5 The volume of air sampled is converted to standard conditions of of 25°C and 760 mm Hg.

$$V_s = V \times \frac{P}{760} \quad \frac{298}{T+273}$$

where:

V_s = volume of air in liters at 25°C and 760 mm Hg

V = volume of air in liters as measured

P = Barometric pressure in mm Hg

T = Temperature of air in degree centigrade

10.6 The concentration of the organic solvent in the air sampled can be expressed in mg per m^3, which is numerically equal to µg per liter of air

$$mg/m^3 = \mu g/\ell = \frac{\text{total mg (Section 10.4) x 1000 (µg/mg)}}{V_s}$$

10.7 Another method of expressing concentration is ppm, defined as µℓ of compounds per liter of air

$$\text{ppm} = \mu\ell \text{ of compound}/V_s$$

$$\text{ppm} = \frac{\mu\ell \text{ of compound}}{V_s} \times \frac{24.45}{MW}$$

where:

24.45 = molar volume at 25°C and 760 mm Hg

MW = molecular weight of the compound (Table 1)

11. References

11.1 White, L.D., D.G. Taylor, P.A. Mauer, and R.E. Kupel, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," *Amer. Ind. Hyg. Assoc. J.*, 31:225 (1970).

11.2 Young, D.M. and A.D. Crowell, Physical Adsorption of Gases, Butterworths, London, 1962, pp. 137-146.

11.3 Federal Register, 37 (#202), 22139-22142 (October 18, 1972).

11.4 NIOSH Contract HSM-99-72-98, Scott Research Laboratories, Inc., "Collaborative Testing of Activated Charcoal Sampling Tubes for Seven Organic Solvents," pp. 4-22, 4-27 (1973).

TABLE I

PARAMETERS ASSOCIATED WITH P&CAB ANALYTICAL METHOD NO. 127

Organic Solvent	Method Classification	Detection limit (mg/sample)	Sample Volume (ℓ) Minimum[a]	Maximum[b]	GC Column Temperature(°C)	Molecular Weight
Acetone	D	-	0.5	7.7	60	58.1
Benzene	A	0.01	0.5	55	90	78.1
Carbon tetrachloride	A	0.20	10	60	60	154.0
Chloroform	A	0.10	0.5	13	80	119
Dichloromethane	D	0.05	0.5	3.8	85	84.9
p-Dioxane	A	0.05	1	18	100	88.1
Ethylene dichloride	D	0.05	1	12	90	99.0
Methyl ethyl ketone	B	0.01	0.5	13	80	72.1
Styrene	D	0.10	1.5	34	150	104
Tetrachloroethylene	B	0.06	1	25	130	166
1,1,2-trichloroethane	B	0.05	10	97	150	133
1,1,1-trichloroethane (Methyl Chloroform)	B	0.05	0.5	13	150	133
Trichloroethylene	A	0.05	1	17	90	131
Toluene	B	0.01	0.5	22	120	92.1
Xylene	A	0.02	0.5	31	100	106

(a) Minimum volume, in liters, required to measure 0.1 times the OSHA standard

(b) These are breakthrough volumes calculated with data derived from a potential plot (reference 11.2) for activated coconut charcoal. Concentrations of vapor in air at 5 times the OSHA standard (reference 11.3) or 500 ppm, whichever is lower, 25°C, and 760 torr were assumed. These values will be as much as 50% lower for atmospheres of high humidity. The effects of multiple contaminants have not been investigated, but it is suspected that less volatile compounds may displace more volatile compounds (See 3.1 and 3.2)

TABLE II

CHEMICALS WHICH HAVE GREATER THAN 80%
DESORPTION EFFICIENCY BUT HAVE NOT BEEN
THOROUGHLY TESTED BY NIOSH

Class E (Proposed)

Acrylonitrile
Allyl glycidyl ether
n-Amyl acetate
2-Butoxyethanol
n-Butyl acetate
n-Butyl alcohol
n-Butylglycidyl ether
Chlorobenzene
Cyclohexane
Cyclohexanone
o-Dichlorobenzene
p-Dichlorobenzene
Diethyl ether
N,N-Dimethyl aniline
Epichlorohydrin
2-Ethoxylethyl acetate
Ethyl acetate
Ethylbenzene
Ethyl butyl ketone
Fufural
Heptane
Hexane
Isoamyl acetate
Isobutyl acetate
Isobutyl alcohol
Isoctane
Isophorone
Isopropyl acetate
Isopropyl glycidyl ether
2,6-Lutidine
Methyl acetate
Methyl acrylate
Methyl n-butyl ketone
Methyl ethyl ketone
Methyl isobutyl ketone
Methyl methacrylate
α-Methyl styrene
p-Methyl styrene
n-Octane
3-Octanone
Pentane
2-Pentanone
α-pinene
n-Propyl acetate
1,1,2,2-Tetrachloroethane
Tetrahydrofuran
Trichlorotrifluoroethane (Freon 113)

Recommended Sample Size = 10ℓ

AROMATIC AMINES[1] IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Aromatic Amines[1]	**Method No.:**	P&CAM 168
Matrix:	Air	**Range:**	0.01-14 mg/ sample
Procedure:	Adsorption on silica gel; elution by ethanol; GC analysis		
Date Issued:	11/1/73	**Precision:**	$2\sigma = \pm 9\%$
Date Revised:	7/15/74	**Classification:**	D (Operational)

1. **Principle of the Method**

   1.1 A known volume of air is drawn through a tube containing silica gel to trap the aromatic amines present.

   1.2 The silica gel in the tube is transferred to a glass-stoppered tube and treated with ethanol.

   1.3 An aliquot of the desorbed aromatic amines in ethanol is injected into a gas chromatograph.

   1.4 Peak areas are determined and compared with calibration curves obtained from the injection of standards.

2. **Range and Sensitivity**

   2.1 The lower limit of this method using a flame ionization detector is 0.01 mg/sample of any one compound when the analyte is desorbed with 5 ml ethanol and a 10-μl aliquot is injected into the gas chromatograph. Sensitivity for p-nitroaniline is 5 times less.

   2.2 The upper limit is at least 14 mg/sample. This is a minimum amount of aniline which the large section (700 mg) and the center section (150 mg silica gel) of the sampling tube will retain before 2% of the sample is found on the third (150 mg) section after 8 hours of sampling (200 ml/min high humidity air containing 150 mg/m^3 aniline). The corresponding upper limit for sampling in the reverse direction through the tube is 3.5 mg/sample. The less volatile substituted anilines have higher upper limits than aniline.

3. **Interferences**

   3.1 The most common possible sampling interference is water vapor. The sampling tube has been designed so that 96 liters of high humidity air can be sampled over an 8-hour period at 200 ml/min without displacement of the collected aromatic amines by water vapor.

   3.2 Any compound which has nearly the same retention time as one of these aromatic amines at the gas chromatograph analytical conditions described in this method is an interference. This type of interference often can be overcome by changing the operating conditions of the gas chromatograph or selecting another column. Retention time data on a single column, or even on a number of columns, cannot be considered as conclusive proof of chemical identity

[1]The list of aromatic amines for which this method has been specifically developed is given in Table 1.

in all cases. For this reason it is important that whenever practical a sample of the bulk compound or mixture be submitted at the same time as the sample tube (but shipped separately) so that chemical identification can be made by other means.

4. **Precision and Accuracy**

4.1 The accuracy of the method depends upon collection efficiencies and desorption efficiencies. If a negligible amount of aromatic amine is detected on the backup section, the collection efficiency of the tube must be essentially 100%. Desorption efficiencies for the range of 1-8 mg have been found to be 100% within experimental error of ± 5%.

4.2 Precision of the analysis is quite dependent upon the precision and sensitivity of the technique used to quantitate gas chromatographic peaks of samples and standards. Electronic digital integrators with baseline correction capabilities can be used to maximize analytical precision, particularly at lower concentrations.

4.3 Precision of preparing chemical standards can be ± 1%.

4.4 The precision of the overall method, $2\sigma = \pm 9\%$, has been determined from eight consecutive identical samples taken with a personal sampling pump.

4.5 Analytical precision can be improved by reducing or eliminating the error associated with syringe injection into the gas chromatograph. This is best accomplished by the addition of internal standard to the ethanol used to both prepare standards and elute samples from the silica gel. Therefore, it is recommended that about 0.1% solution of n-heptanol in ethanol be used. For isothermal analyses at temperatures above 120°C, n-octanol may be preferable.

5. **Advantages and Disadvantages of the Method**

5.1 The sampling method uses a small, portable device involving no liquids. Taking the effect of humidity into account, a sample of up to 8 hours can be taken for an average work day concentration or a 15-minute sample can be taken to test for excursion concentrations. Desorption of the collected sample is simple and is accomplished with a solvent with low toxicity. The analysis is accomplished by a quick instrumental method. Most analytical interferences which occur can be eliminated by altering gas chromatographic conditions. Several aromatic amines can be collected and analyzed simultaneously; this is useful where the composition of the aromatic amine vapors may not be known.

5.2 A major disadvantage of the method is the limitation on its precision due to the use of personal sampling pumps currently available. After initial adjustment of flow any change in the pumping rate will affect the volume of air actually sampled. Furthermore, if the pump used is calibrated for one tube only, as is often the case, the precision of the volume of air sampled will be limited by the reproducibility of the pressure drop across the tubes.

6. **Apparatus**

6.1 One or more personal sampling pumps whose flow can be set at and maintained at 1 liter/min for 15 min or 200 ml/min for 8 hours.

6.2 Pyrex glass sampling tubes of the dimensions shown in Figure 1 packed with three sections of 45/60 mesh silica gel. The weights of the sections in order are 700 mg, 150 mg, and 150 mg. The silica gel should be the equivalent of Silica Gel D-08, Chromatograph Grade, Activated and Fines Free, 45/60 Mesh, from Applied Science Laboratories, Inc., State College, Pa. Plugs of 100 mesh stainless steel screen are used to contain the silica gel sections. These plugs of negligible pressure drop are prepared from 11-mm diameter discs pushed into an

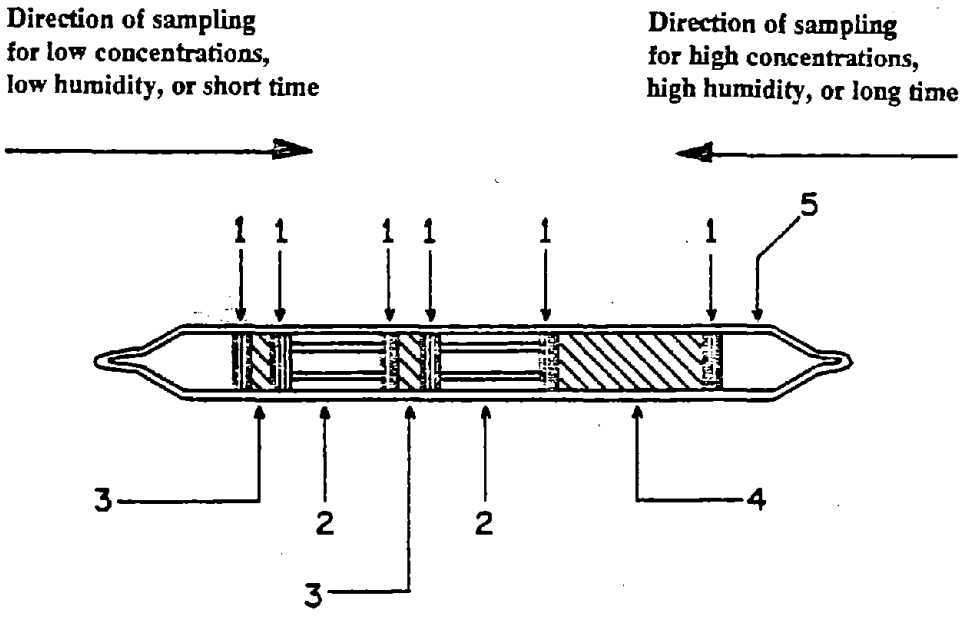

FIGURE 1. Silica gel sampling tube for aromatic amines. (1) 100 mesh stainless steel screen plugs; (2) 12-mm glass tube separator; (3) 150-mg silica gel section, 45/60 mesh; (4) 700-mg silica gel section, 45/60 mesh; (5) 8-mm I. D. glass tube.

8-mm I.D. tube with a 7-mm O.D. rod. Pieces of Pyrex tubing 7 mm O.D. by 12 mm long and located between the sorbent sections greatly reduce migration of the sample throughout the tube prior to analysis. The ends of each tube should be flame sealed after packing to prevent contamination before sampling. The pressure drop of such tubes should not exceed 13 in of water at 1 liter/min or 2.5 in of water at 200 ml/min air flows.

6.3 Gas chromatograph equipped with a flame ionization detector. Linear temperature programming capability is desirable but not essential.

6.4 Column (4 ft × ⅛ in O.D., stainless steel) packed with Silicone OV-25 liquid phase, 10% on 80/100 mesh Supelcoport (or equivalent support). A column (2 ft × ⅛ in O.D.) packed with Chromosorb 103 (80/100 mesh) can be used for all the amines except p-nitroaniline.

6.5 Recorder and some method for determining peak height or area.

6.6 Glass-stoppered tubes or flasks, 2 ml and 10 ml.

6.7 Syringes, 10 μl.

6.8 Pipettes and volumetric flasks for preparation of standard solutions.

7. Reagents

7.1 Ethanol, 95%.

7.2 n-Heptanol and n-octanol, reagent grade.

7.3 Reagent grade aromatic amines standards.

7.4 Bureau of Mines Grade A helium.

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

8. Procedure

8.1 **Cleaning of equipment:** All glassware used for the laboratory analysis is detergent washed followed by tap and distilled water rinses.

8.2 **Calibration of personal pumps:** Each pump must be calibrated with a representative tube in the line to minimize errors associated with uncertainties in the sample volume collected.

8.3 **Collection and Shipping of Samples**

8.3.1 Immediately before sampling, the ends of the tube should be broken so as to provide an opening at least one half the internal diameter of the tube.

8.3.2 The desired sampling direction is chosen, the initial section marked with a permanent marker, and tubing from the sampling pump attached to the other end. For low concentrations, low humidity, and short-term samples, the smaller (150 mg) section is used for the initial section. For expected high concentrations, high humidity, and long-term samples, the largest (700 mg) section is used for the initial section. See Table 1 footnotes. Sampled air should not pass through any hose or tubing before entering the sampling tube.

8.3.3 The atmosphere is sampled at the desired flow rate for the desired period of time. Recommended sampling volumes based on sensitivity and breakthrough studies are given in Table 1. The flow rate and sampling time or the volume of sampled air must be measured as accurately as possible.

8.3.4 The temperature, pressure, and humidity of the atmosphere being sampled is measured and recorded.

8.3.5 The sampling tubes are capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.6 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube is labeled as a blank.

8.3.7 Capped tubes should be packed tightly before shipping to minimize tube breakage during shipping.

8.3.8 Samples of the bulk liquids or solids from which the aromatic amine vapors arise should be submitted to the laboratory also, but **not** in the same container as the air samples or blank tubes.

8.3.9 Storage: Tubes after sampling should be tightly capped and not subjected to extremes of high temperature or low pressure, if avoidable.

8.4 **Analysis of Samples**

8.4.1 Preparation of samples: By removing and discarding the stainless steel plugs and glass spacers the silica gel sections are transferred to separate glass-stoppered tubes or flasks (2 ml for the smaller sections and 10 ml for the larger section). Note or mark which tubes contain the initial section, the backup section, and the third section. These are analyzed separately.

8.4.2 Desorption of samples: Prior to analysis, ethanol containing 0.1% n-heptanol internal standard is pipetted into each flask — 5 ml for the large section and 1 ml for all other sections. Tests indicate that desorption is complete in 30 min if the sample is stirred or shaken occasionally.

8.4.3 Gas chromatograph conditions: Typical operating conditions for the gas chromatograph. are: carrier flow (25 ml He/min); injection port (150°C); flame ionization detector (250°C, 50 ml/min H_2, 470 ml/min air); oven temperature program (100°C for 4 min, then increase at 8°C/min to 225°C).

8.4.4 An aliquot of the sample is injected into the gas chromatograph. With an internal standard in the eluent, direct injection of up to 10 μl with a microliter syringe is acceptably precise. At least duplicate injections of the same sample or standard are recommended.

8.4.5 The areas of the sample peak and the internal standard peak are measured by an electronic integrator or some other suitable method of area measurement. The ratio of these areas is calculated and used to determine sample concentration in the eluent by using a standard curve prepared as discussed below.

9. **Calibration and Standards**

9.1 For accuracy in the preparation of standards, it is recommended that one standard be prepared in a relatively large volume and at a high concentration. Aliquots of this standard can then be diluted to prepare other standards. The solvent and diluent used must be the same ethanol/n-heptanol mixture used for the elution of the samples. For example, to prepare a 100-ml standard corresponding to a 96-liter sample of air containing 95 mg/m^3 of aniline (density = 1.022 g/ml) desorbed with 5 ml,

$$\frac{(95\ \text{mg/m}^3)\ (0.096\ \text{m}^3)}{5\ \text{ml}} \times \frac{100\ \text{ml}}{1.022\ \text{mg}/\mu\text{l}} = 178\ \mu\text{l}$$

of aniline is added to a 100-ml volumetric flask and diluted to the mark. The resulting concentration is

$$\frac{(178\ \mu l)\ (1.022\ mg/\mu l)}{100\ ml} = 1.82\ mg/ml$$

If 2 ml of this solution is diluted to 10 ml in a volumetric flask with the ethanol/n-heptanol mixture, the resulting concentration is

$$(1.82\ mg/ml) \times \frac{2\ ml}{10\ ml} = 0.365\ mg/ml$$

When microliter pipettes are used instead of microliter syringes, it is better to prepare standards using a round number of microliters (e.g., 200 μl aniline instead of 178 μl). For solids, the amount of compound used for the first standard should be weighed on an analytical balance. A series of standards is prepared varying in concentration over the range of interest.

9.2 The standards prepared as above should be analyzed under the same GC conditions and during the same time period as the unknown samples. This will minimize the effect of day-to-day variations of the flame ionization detector response.

9.3 A standard curve is prepared for each compound by plotting ratios of peak areas of the compound to the internal standard against the concentration of the compound. From the resulting curve the concentration of an eluted sample is determined. This concentration (in mg/ml) is then converted to total sample weight by multiplying by the amount of ethanol used for that section (1 or 5 ml).

10. **Calculations**

10.1 Corrections for the blank must be made for each sample.

$$\text{Correct mg} = mg_s - mg_b$$

where:

mg_s = mg found in front section of sample tube

mg_b = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.2 Add the corrected amounts present in the front and backup sections of the same sample tube to determine the total measured amount (w) in the sample.

10.3 Convert the volume of air sampled to standard conditions of 25°C and 760 mm Hg.

$$V_s = V \times \frac{P}{760} \times \frac{298}{T + 273}$$

where:

V_s = volume of air in liters at 25°C and 760 mm Hg

V = volume of air in liters as calculated (sampling time × correct flow rate)

P = barometric pressure in mm Hg

T = temperature of air in degrees centigrade

10.4 The concentration of the organic solvent in the air sampled can be expressed in mg per m^3, which is numerically equal to μg per liter of air

$$mg/m^3 = \mu g/l = \frac{w\ (mg) \times 1000\ (\mu g/mg)}{V_s}$$

10.5 Another method of expressing concentration is ppm, defined as μl of compound vapor per liter of air

$$\text{ppm} = \mu\text{l of vapor}/V_s$$

$$\text{ppm} = \frac{\text{v } (\mu\text{g})}{V_s} \times \frac{24.45 \text{ l/mole}}{\text{MW}}$$

where:

24.45 l/mole = molar volume at 25°C and 760 mm Hg

MW = molecular weight of the compound (g/mole)

11. Reference

11.1 Campbell, E. E., G. O. Wood, and R. G. Anderson, Los Alamos Scientific Laboratory Progress Reports LA-5104-PR, LA-5164-PR, LA-5308-PR, LA-5389-PR, LA-5484-PR, and LA-5634-PR, Los Alamos, New Mexico, November 1972, January 1973, June 1973, August 1973, December 1973, and June 1974.

TABLE I

Aromatic amines for which the method has been tested

	OSHA standard[a]		Recommended sample volumes (liters)	
	(ppm)	(mg/m³)	Minimum[b]	Maximum[c]
Aniline	5	19	5	150
N,N-Dimethylaniline	5	25	5	190
o-Toluidine	5	22	5	300
2,4-Xylidine	5	25	5	430
o-Anisidine	0.1	0.5	250	35,800
p-Anisidine	0.1	0.5	250	33,000
p-Nitroaniline	1	6	80	12,100

[a]Taken or calculated from Federal Register, 37: #202, 22139 (18 October 1972).

[b]Based on analytical sensitivity and 0.1 OSHA standard detection when using the large section as the initial section (see 2.1). When the smaller section is used as the initial section, divide these minimum volumes by 5.

[c]Based on breakthrough studies at high humidities and a concentration of 5 times the OSHA standard when using the large section as the initial section. When the smaller section is used as the initial section, divide these maximum volumes by 5.

Cresol, All Isomers

Analyte:	Cresol, all isomers	Method No.: S167
Matrix:	Air	Range: 10.54-42.2 mg/cu m
OSHA Standard:	5 ppm (22 mg/cu m)-skin	Precision ($\overline{CV}_T$): 0.068
Procedure:	Adsorption on silica gel, desorption with acetone; GC	Validation Date: 8/1/75

1. Principle of the Method (Reference 11.1)

   1.1 A known volume of air is drawn through a silica gel tube to trap the organic vapors present.

   1.2 The silica gel in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with acetone.

   1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

   1.4 The combined areas of the resulting two peaks are determined and compared with areas obtained for standards.

2. Range and Sensitivity

   2.1 This method was validated over the range of 10.54-42.2 mg/cu m at an atmospheric temperature and pressure of 22°C and 760 mm Hg, using a 20-liter sample. Under the conditions of sample size (20 liters) the probable useful range of this method is 5-60 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 1-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

   2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the silica gel tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the silica gel tube was found to hold at least 1.87 mg of analyte when a test atmosphere containing

42.2 mg/cu m of analyte in air was sampled at 0.185 liter per minute for 240 minutes. (The silica gel tube consists of two sections of silica gel separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interferences

3.1 Silica gel has a high affinity for water, so organic vapors will not be trapped efficiently in the presence of a high relative humidity. This effect may be important even though there is no visual evidence of condensed water in the silica gel tube.

3.2 When compounds other than the isomers of cresol are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample. Since acetone is used to desorb the analyte from the silica gel, it is not possible to measure acetone in the sample.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 10.54-42.2 mg/cu m was 0.068. This value corresponds to a 1.5 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 4.2% lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result from paragraph 10.5.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the silica gel tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Silica gel tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh silica gel separated by a 2-mm portion of urethane foam. The adsorbing section contains approximately 150 mg of silica gel, the backup section, approximately 75 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery pipets.

6.9 Volumetric flasks: convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality acetone.

7.2 Cresol (all isomers) - prepare a standard mixture of the isomers by adding together 20 g of the ortho, 40 g of the meta, and 30 g of the para isomers and mix.

7.3 Prepurified hydrogen.

7.4 Filtered compressed air.

7.5 Purified nitrogen.

7.6 n-Hexane, reagent grade.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative silica gel tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of silica gel is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The silica gel tube should be placed in a vertical direction during sampling to minimize channeling through the silica gel.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the silica gel tube.

8.3.5 A sample size of 20 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm 5\%$.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The silica gel tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the silica gel tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each silica gel tube is scored with a file in front of the first section of silica gel and broken open. The glass wool and the silica gel in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of acetone is pipetted into each sample container. Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 230°C injector temperature
5. 250°C manifold temperature (detector)
6. 200°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush method.

8.4.5 Measurement of area. Although there are three isomers of cresol, there are only two peaks on the gas chromatogram, because the meta and para isomers have the same retention time. The total area of the two sample peaks is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of silica gel to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of silica gel is used.

8.5.2 Procedure for determining desorption efficiency. Silica gel equivalent to the amount in the first section of the sampling tube (approximately 150 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This silica gel must be from the same batch as that used in obtaining the samples and can be obtained from unused silica gel tubes. The open end is capped with Parafilm.

A standard solution is prepared by placing 1100 mg of the mixture of the isomers of cresol in a 10-ml volumetric flask and making it up to volume with n-hexane. A known amount of the standard solution is injected directly into the silica gel with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

The amount injected is equivalent to that present in a 20-liter air sample at the selected level. Six tubes at each of the three levels are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the silica gel. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of acetone with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) is dependent on the amount of analyte collected on the silica gel. The desorption efficiency equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight recovered (mg)}}{\text{Weight added (mg)}}$$

The desorption efficiency is dependent on the amount of analyte collected on the silica gel. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/1.0 ml acetone, because samples are desorbed in this amount of acetone. A series of standards, varying in concentration over the range of interest, are prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/1.0 ml versus total peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each combined peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/1.0 ml acetone and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (See Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

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11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

GENERAL PROCEDURE FOR METALS

Measurements Research Branch

Analytical Method

Analyte:	Trace Metals (Tables 1 and 2)	**Method No.:**	P&CAM 173
Matrix:	Air	**Range:**	Varies with analyte (Table 2)
Procedure:	Filter collection, atomic absorption analysis	**Precision:**	3% RSD (Analytical)
Date Issued:	9/17/73		
Date Revised:	3/11/77	**Classification:**	D (Operational)

1. Principle of the Method

1.1 This procedure describes a general method for the collection, dissolution and determination of trace metals in industrial and ambient airborne material. The samples are collected on membrane filters and treated with nitric acid to ash the organic matrix and to dissolve the metals present in the sample. The analysis is subsequently made by atomic absorption spectrophotometry (AAS).

1.2 Samples and standards are aspirated into the appropriate AAS flame. A source of characteristic radiation energy is necessary for each metal. The absorption of this characteristic energy by the atoms of interest in the flame is related to the concentration of the metal in the aspirated sample. The flames and operating conditions for each element are listed in Table 1.

2. Range and Sensitivity

The sensitivity, detection limit, and optimum working range for each metal are given in Table 2. The sensitivity is defined as that concentration of a given element which will absorb 1% of the incident radiation (0.0044 absorbance units) when aspirated into the flame. The detection limit is defined as that concentration of a given element which produces a signal equivalent to two times the standard deviation of the blank signal for aqueous solutions. Detection limits and blank values for real samples may be greater than those given in Table 2 since the blanks resulting from the reagents and the filter material have not been taken into account. The working range for an analytical precision better than 3% is generally defined as those sample concentrations which will absorb greater than 10% of the incident radiation and are in the linear region of the calibration curve. The values for the sensitivity and detection limits are instrument dependent and may vary from instrument to instrument.

3. Interferences

3.1 In atomic absorption spectrophotometry, the occurrence of interference is less common than in many other analytical determination methods. Interferences can occur, however, and when encountered are corrected for as indicated in the following sections. The known interfer-

ences and correction methods for each metal are indicated in Table 1. The methods of standard additions and background monitoring and correction (11.1-11.4) are used to identify the presence of an interference problem. Insofar as possible, the matrix of the samples and standards are matched to minimize the possible interference problems.

3.1.1 Background or non-specific absorption can occur from particles produced in the flame which can scatter the incident radiation causing an apparent absorption signal. Light scattering problems may be encountered when solutions of high salt content are being analyzed. Light scattering problems are most severe when measurements are made at the lower wavelengths (i.e., below about 250 nm). Background absorption may also occur as the result of the formation of various molecular species which can absorb light. The background absorption should be accounted for by the use of background correction techniques (use of D_2 or H_2 continuum or a nearby non-absorbing wavelength) (11.1, 11.6).

3.1.2 Spectral interferences are those interferences which occur as the result of an atom different from that being measured absorbing a portion of the incident radiation. Such interferences are extremely rare in atomic absorption. In some cases, multi-element hollow cathode lamps may cause a spectral interference by having closely adjacent radiation lines from two different elements. In such instances, multi-element hollow cathode lamps should not be used, or the use of more narrow spectral slits or alternate wavelengths may be used to alleviate the problem.

3.1.3 Ionization interferences can occur when easily ionized atoms are being measured. The degree to which such atoms are ionized is dependent upon the atomic concentration and presence of other easily ionized atoms in the sample. Ionization interferences can be controlled by the addition to the sample of a high concentration of another easily ionized element which will buffer the electron concentration in the flame. Typically, 1000 to 2000 μg/ml of an alkali metal (K, Na, Cs) salt is added to sample and standard solutions.

3.1.4 Chemical interferences occur in atomic absorption spectrophotometry when species present in the sample cause variations in the degree to which atoms are formed in the flame. Such interferences may be corrected for by controlling the sample and standard matrix, by using the method of standard additions, or by use of a higher temperature flame (11.2, 11.6).

3.1.5 Physical interferences may result if the physical properties of the samples vary significantly. Changes in viscosity and surface tension can affect the sample aspiration rate and thus cause erroneous results. Sample dilution and/or the method of standard additions are used to correct such interferences. High concentrations of silicates in the sample can cause an interference for many of the elements and may cause aspiration problems. No matter what elements are being measured, if large amounts of silicates are extracted from the samples, the samples should be allowed to stand for several hours and centrifuged or filtered to remove the silicates.

3.2 This procedure describes a generalized method for sample preparation which is applicable to the majority of samples of interest. There are, however, some relatively rare chemical forms of a few of the elements listed in Table 1 which will not be dissolved by this procedure. If such chemical forms are suspected, results obtained using this procedure should be compared with those obtained using an appropriately altered dissolution procedure. Alternatively, the results may be compared with values obtained utilizing a non-destructive technique which does not require sample dissolution (e.g., X-ray fluorescence, activation analysis).

4. **Precision and Accuracy**

4.1 The relative standard deviation of the analytical measurement is approximately 3% when measurements are made in the ranges listed in Table 2. The overall relative standard deviation will be somewhat larger than this value due to errors associated with the sample collection and preparation steps.

4.2 No data are presently available on the accuracy of this method for actual air samples.

5. **Advantages and Disadvantages of the Method**

5.1 The sensitivity is adequate for all metals in air samples provided an adequate volume of air is sampled.

5.2 A disadvantage of the method is that approximately 2 ml of solution is necessary for each metal determination. Also, the necessary dilution limits the detection of small quantities of analyte or replicate analysis of several elements per sample.

6. **Apparatus**

6.1 Sampling Equipment. The sampling unit for the collection of personal air samples has the following components:

6.1.1 The filter unit, consisting of the filter media (6.2) and appropriate cassette filter holder, either a 2- or 3-piece filter cassette (Millipore Filter Corporation, Bedford, Mass., or equivalent).

6.1.2 A personal sampling pump of sufficient capacity to maintain a face velocity of 2.6 cm/sec (1-2 lpm using a 37-mm filter). This pump must be calibrated so the volume of air sampled can be measured to an accuracy of $\pm$ 5%. The pump must be calibrated with a representative filter unit in the line.

6.1.3 Thermometer.

6.1.4 Manometer.

6.1.5 Stopwatch.

6.1.6 Various clips, tubing, spring connectors, and belt for connecting sampling apparatus to worker being sampled.

6.2 Cellulose ester membrane filter, 0.8-μm pore size, 37-mm (Millipore Type AA or equivalent).

6.3 Glassware, borosilicate. Before use, all glassware must be cleaned in 1:1 diluted nitric acid and rinsed several times with distilled water.

6.3.1 125-ml Phillips or Griffin beakers with watch glass covers.

6.3.2 15-ml graduated centrifuge tubes.

6.3.3 10-ml volumetric flasks.

6.3.4 100-ml volumetric flasks.

6.3.5 1-liter volumetric flasks.

6.3.6 125-ml polyethylene bottles.

6.3.7 Additional auxiliary glassware such as pipettes and different size volumetric glassware will be required depending on the elements being determined and the dilutions required to have sample concentrations above the detection limit and in the linear response range (i.e., see Table 2). All pipettes and volumetric flasks required in this procedure should be calibrated class A volumetric glassware.

6.4 Hotplate (suitable for operation at 140°C).

6.5 **Equipment for Analysis**

6.5.1 Atomic absorption spectrophotometer, with burner heads for air-acetylene and nitrous oxide-acetylene flames.

6.5.2 Hollow cathode or electrodeless discharge lamps, for each metal and a continuum lamp (D_2 or H_2).

6.5.3 Two stage regulators, for air, acetylene, and nitrous oxide.

6.5.4 Heating tape and rheostat, for nitrous oxide regulator (second regulator stage and connecting hose to the instrument should be heated to approximately 60°C to prevent freeze-up).

6.6 **Supplies**

6.6.1 Acetylene gas (cylinder), of a grade specified by the manufacturer of the instrument employed. (Replace cylinder when pressure decreases below 100 psi.)

6.6.2 Nitrous oxide gas (cylinder).

6.6.3 Air supply, with a minimum pressure of 40 psi, filtered to remove oil and water.

7. **Reagents**

7.1 Purity. ACS analytical reagent grade chemicals or equivalent shall be used in all tests. References to water shall be understood to mean double distilled water or equivalent. Care in selection of reagents and in following the listed precautions is essential if low blank values are to be obtained.

7.2 Concentrated nitric acid (68-71%), redistilled, specific gravity 1.42.

7.3 Standard stock solutions (1000 μg/ml) for each metal in Table 1, commercially prepared or prepared per instrument manufacturer's recommendations.

7.4 Lanthanum nitrate [$La(NO_3)_3 \cdot 6H_20$].

7.5 Cesium nitrate ($CsN0_3$).

8. **Procedure**

8.1 **Cleaning of Equipment**

8.1.1 Before initial use, glassware is cleaned with a saturated solution of sodium dichromate in concentrated sulfuric acid (Note: Do not use for chromium analysis) and then rinsed thoroughly with warm tap water, concentrated nitric acid, tap water, and deionized water, in that order, and then dried.

8.1.2 All glassware is soaked in a mild detergent solution immediately after use to remove any residual grease or chemicals.

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, it is not necessary to use the chromic acid cleaning solution.

8.2 **Collection and Shipping of Samples**

8.2.1 Ambient atmospheric particulate matter and industrial dusts and fumes are sampled with cellulose membrane filters. Sample flow rate is monitored with a calibrated rotameter (11.5) or the equivalent. The flow rate, ambient temperature, and barometric pressure are recorded at the beginning and the end of the sample collection period.

8.2.2 For personal sampling, 37-mm diameter filters in holders are used. The personal sampling pumps for this application are operated at 1.5 lpm. In general, a 2-hour

sample at 1.5 lpm will provide enough sample to detect the elements sought at air concentrations of 0.2 × TLV.

8.2.3 After sample collection is complete, plug the openings of the cassette and submit the sampling unit to the laboratory. Losses of sample due to overloading (>2 mg) of the filter must be avoided.

8.2.4 Filter samples should be sealed in individual plastic filter holders for storage and shipment.

8.3 **Preparation of Samples**

8.3.1 The samples and blanks (minimum of 1 filter blank for every 10 filter samples) are transferred to clean 125-ml Phillips or Griffin beakers and 6.0 ml HNO_3 is added. Antimony samples are ashed in 6.0 ml of a 5:1 mixture of HNO_3:H_2SO_4. Each beaker is covered with a watch glass and heated on a hot plate (140°C) in a fume hood until the sample dissolves and a slightly yellow solution is produced. Approximately 4 hours of heating will be sufficient for most air samples. However, subsequent additions of HNO_3 may be needed to completely ash and destroy high concentrations of organic material, and under these conditions longer ashing times will be needed. Once the ashing is complete as indicated by a clear solution in the beaker, the watch glass is removed and the sample is allowed to evaporate to near dryness (approximately 0.5 ml).

8.3.2 Remove the beaker from the hot plate, cool, and add 1 ml HNO_3 and 2-3 ml of distilled H_2O. For lead samples, concentrated HCl is used instead of HNO_3. The solution is quantitatively transferred with distilled water to a 10-ml volumetric flask. If any elements are being determined which require the ionization buffer, 0.2 ml of 50 mg/ml Cs is added to the volumetric flask (see Table 1, footnote d). If any elements requiring the releasing agent are being determined, 0.2 ml of 50 mg/ml La is added to each volumetric flask (see Table 1, footnote 3). The samples are then diluted to volume with water.

8.3.3 The 10-ml solution may be analyzed directly for any element of very low concentration in the sample. Aliquots of this solution may then be diluted to an appropriate volume for the other elements of interest present at higher concentrations. (Note: Approximately 2 ml of solution are required for each element being analyzed.) The dilution factor will depend upon the concentration of elements in the sample and the number of elements being determined by this procedure.

8.4 **Analysis of Samples**

8.4.1 Set the instrument operating conditions as recommended by the manufacturer. The instrument should be set at the radiation intensity maximum for the wavelength listed in Table 1 for the element being determined.

8.4.2 Standard solutions should match the sample matrix as closely as possible and should be run in duplicate. Working standard solutions, prepared fresh daily, are aspirated into the flame and the absorbance recorded. Prepare a calibration graph as described in Section 9.2.3. (Note: All combustion products from the AA flame must be removed by direct exhaustion through the use of a good separate flame ventilation system.)

8.4.3 Blank filters must be carried through the entire procedure each time samples are analyzed.

8.4.4 Aspirate the appropriately diluted samples directly into the instrument and record the absorbance for comparison with standards. Should the absorbance be above the calibration range, dilute an appropriate aliquot to 10 ml. Aspirate water between each sample. A mid-range standard must be aspirated with sufficient frequency (i.e.,

once every 5 samples) to assure the accuracy of the sample determinations. To the extent possible, all determinations are to be based on replicate analysis.

9. Calibration and Standards

9.1 Ionization and chemical interference suppressants

9.1.1 Lanthanum solution (50 mg/ml). Dissolve 156.32 g of lanthanum nitrate [$La(NO_3)_3 \cdot 6H_2O$] in 2% (v/v) HNO_3. Dilute to volume in a 1-liter volumetric flask with 2% (v/v) HNO_3. When stored in a polyethylene bottle, this solution is stable for at least one year.

9.1.2 Cesium solution (50 mg/ml). Dissolve 73.40 g of cesium nitrate ($CsNO_3$) in distilled water. Dilute to volume in a 1-liter volumetric flask with distilled water. When stored in a polyethylene bottle this solution is stable for at least one year.

9.2 Standard metal solutions

9.2.1 Dilute standards (100 μg metal/ml). Pipet 10 ml of the stock (1000 μg metal/ml; Section 7.3) into a 100-ml volumetric flask, add 10 ml HNO_3 and dilute to volume with distilled water. For antimony standards, 5 ml H_2SO_4 is added with the HNO_3. Lead standards require 10 ml HCl instead of 10 ml HNO_3. Prepare these standards fresh weekly. (Note: Silver standards must be stored in amber bottles away from direct light.)

9.2.2 Working standards. Working standards for each metal of interest are prepared by dilution of the dilute standards (9.2.1) or the stock standards (7.3) such that the final acid concentration is the same for the samples and standards (i.e., 10% v/v HNO_3 in most cases). Lanthanum or cesium is added to samples and standards as indicated in Table 1 such that the final concentration is 1000 μg La or Cs/ml. Concentrations of the working standards should cover the range for the metal of interest (Table 2). Prepare these solutions fresh daily.

9.2.3 The standard solutions are aspirated into the flame and the absorbance (or concentration) recorded. If the instrument used displays transmittance, these values must be converted to absorbance. A calibration curve is prepared by plotting absorbance (units) versus metal concentration. The best fit curve (calculated by linear least square regression analysis) is fitted to the data points. This line or the equation describing the line is used to obtain the metal concentration in the samples being analyzed.

9.2.4 To insure that the preparation procedure is being properly followed, clean membrane filters are spiked with known amounts of the elements being determined by adding appropriate amounts of the previously described standards and carried through the entire procedure. The amount of metal is determined and the per cent recovery calculated. These tests will provide recovery and precision data for the procedure as it is carried out in the laboratory for the soluble compounds of the elements being determined.

9.2.5 Analysis by the method of standard additions. In order to check for interferences, samples are initially and periodically analyzed by the method of standard additions and the results compared to those obtained by the conventional analytical determination. For this method the sample is divided into three 2-ml aliquots. To one of the aliquots an amount of metal approximately equal to that in the sample is added. To another aliquot twice this amount is added. (Note: Additions should be made by micropipetting techniques such that the volume does not exceed 1% of the original aliquot volume, i.e., 10 μl and 20 μl additions to a 2-ml aliquot.) The solutions are then analyzed and the absorbance readings are plotted against metal added to the

original sample. The line obtained from such a plot is extrapolated to 0 absorbance and the intercept on the concentration axis is taken as the amount of metal in the original sample (11.2). If the result of this determination does not agree to within 10% of the values obtained with the procedure described in section 9.2.3, an interference is indicated and standard addition techniques should be utilized for sample analysis.

10. Calculations

10.1 The uncorrected volume collected by the filter is calculated by averaging the beginning and ending sample flow rates, converting to cubic meters and multiplying by the sample collection time. The formula for this calculation is

$$V = \frac{(F_B + F_E)\, t}{2000}$$

where:

V = sample volume (m^3)

F_B = sample flow rate at beginning of sample collection (1pm)

F_E = sample flow rate at end of sample collection (1pm)

t = sample collection time (minutes)

10.2 After any necessary correction for the blank has been made, metal concentrations are calculated by multiplying the micrograms of metal per ml in the sample aliquot by the aliquot volume and dividing by the fraction which the aliquot represents of the total sample and the volume of air collected by the filter:

$$\mu g \text{ metal}/m^3 = \frac{(C \times V_A) - B}{V \times F}$$

where:

C = concentration (μg metal/ml) in the aliquot

V_A = volume of aliquot (ml)

B = total μg of metal in the blank

F = fraction of total sample in the aliquot used for measurement (dimensionless)

V = volume of air sampled (m^3)

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BENZENE-SOLUBLE COMPOUNDS IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte: Benzene Solubles	Method No.: P&CAM 217
Matrix: Air particulates trapped on silver membrane and glass fiber filters	Range: 20 μg/sample
Procedure: Ultrasonic extraction with benzene, aliquot evaporated to dryness and weighed	Precision (CV): 0.02 (analytical) for 1 mg; 0.23 (analytical)for 20 μg
Date Issued: 1/29/76	Classification: D (Operational)
Date Revised:	

1. **Principle of the Method**

   Particulate matter suspended in air is collected on a filter. The filter is extracted with benzene with ultrasonic agitation. An aliquot of the extract is evaporated to dryness and the residue is weighed.

2. **Range and Sensitivity**

   The limit of detection is estimated to be 20 μg of benzene-soluble material in a filter sample; this value is two times the standard deviation of values determined for six blank filters. For a 300-liter air sample the limit of detection is, therefore, 0.067 mg/m^3. The range of the method extends upward to any weighable amount greater than 20 μg per sample.

3. **Interferences**

   By definition, the method is inherently free of interferences that could occur in the particulate material collected on a filter. Errors may be caused by extraneous dust picked up in handling the filter or by changes in humidity or temperature during weighing. These errors may be avoided if the sample is properly protected and if temperature and humidity are controlled.

4. Precision and Accuracy

4.1 The analytical precision is dependent upon the amount of residue remaining to be weighed after evaporation of the solvent, as illustrated by the following example. Several benzene extracts of samples of aluminum reduction plant emissions were combined to give a solution containing the equivalent of 1.350 mg of benzene-soluble material per sample; nine aliquots of this solution gave residue weights with a coefficient of variation of 0.02. Benzene extracts of six blank filters gave residue weights with a coefficient of variation of 0.23.

4.2 The accuracy of this method has not been determined.

5. Advantages and Disadvantages

5.1 Ultrasonic agitation has been reported to be more efficient than Soxhlet extraction for dissolving organic materials is particulate samples. For example, the recovery of polycyclic arenes is higher with ultrasonic extraction than with Soxhlet extraction (Reference 11.3).

5.2 A major advantage of the method is that it is simple and direct. The analysis can be made by a technician with minimum training. An experienced technician should be able to analyze a set of 12 samples in 4 hr. If the extraction, evaporation, and weighing are staggered, it should be possible to analyze three sets of 12 samples in an 8-hr day.

5.3 The method is free of interference if temperature and humidity are constant during weighing and if the laboratory atmosphere is dust-free.

5.4 The method is empirical and nonspecific,and measures all substances in a sample that are soluble in benzene. It yields no information on the composition of the benzene-soluble material.

6. Apparatus

6.1 **Air Sampling Equipment**

6.1.1 Glass fiber filters, 37 mm, free of organic binder, with an efficiency of at least 99% as determined by the DOP penetration test.

6.1.2 Silver membrane filters, 37 mm, 0.8 μm pore size, Selas Corporation of America, No. FM-37-(0.8), or equivalent.

6.1.3 Disposable plastic filter holder (cassette) for 37-mm filters, Millipore M000 037 P0, or equivalent. In order to accommodate the two filters, the cassette must be held together with tape or a shrinkable band.

6.1.4 Personal sampling pump capable of operating for 4 hr at 1.5 ℓ/min. The pump should be calibrated with a representative filter assembly in the line. A wet or dry test meter or a glass rotameter capable of measuring the flow rate of 1.5 ℓ/min to within ± 5% may be used for the calibration.

6.2 **Electrobalance.** Cahn Instruments, Model G-2, or equivalent.

6.3 **Vacuum oven.** Thelco Model 19, GCA Precision Scientific, or equivalent.

6.4 **Ultrasonic bath.** Dynasonics Corporation Model NT-201, 90 kHz, 60 W, or equivalent. An ultrasonic bath operating at a lower frequency and having a higher power output may improve extraction efficiency. (See Reference 11.4.). A test tube support is needed for use in the ultrasonic bath.

6.5 Test tubes, 100 mm by 16 mm, with Teflon-lined screw caps.

6.6 Teflon weighing cups, Cahn Instruments No. 2034, or equivalent, approximate tare weight, 60 mg.

6.7 Allihn tubes, fine-porosity fritted glass, 30 mℓ.

6.8 Small glass vials with Teflon-lined screw caps.

6.9 Volumetric pipettes, 1 and 5 mℓ.

6.10 Wood applicator sticks, 6 in. long and 1/16 in. diameter.

6.11 Weighing paper, 3.5 by 4.5 in.

6.12 Tweezers.

7. **Reagents**

7.1 **Benzene, ACS reagent grade.**

7.2 Nitrogen, prepurified.

8. **Procedure**

8.1 **Cleaning of Equipment.** Wash the glassware with detergent solution and rinse with tap water and distilled water. Wash the Teflon weighing cups with reagent grade acetone and allow them to dry.

8.2 Collection and Shipping of Samples

8.2.1 Assemble the filters in the filter holder so that the air being sampled passes first through a glass fiber filter and then through a silver membrane filter. Remove the small plugs from the filter holder and connect the filter holder to the sampling pump by means of an adaptor and a length of tubing. Sample at least 300 liters of air at 1.5 ℓ/min. The optimum sample volume will depend on the type of workroom environment being sampled. Since high concentrations of particulate material or certain types of mists may plug the filters, the flow rate should be checked about once every hour. On completion of sampling, reinsert the small plugs in the inlet and outlet of the filter holder.

8.2.2 With each group of samples prepare at least three blanks consisting of a filter holder with representative filters that have been handled in the same manner as the sample filters, except that no air is drawn through them. The samples and the blanks should be shipped promptly in a light-proof container to prevent photooxidation or damage during transit.

8.3 Analysis of Samples The glass fiber and silver membrane filters are extracted together in the same test tube. At least three sets of blank filters are extracted along with each group of samples.

8.3.1 Extraction

1. Remove the top portion of the filter holder. Hold the bottom portion containing the filters over a piece of weighing paper to catch any particulate material that may fall out. Remove the small plug from the bottom portion of the filter holder and insert an applicator stick through the hole. Gently raise the filters and grasp the unexposed edge with tweezers. Fold the filters in half and then lengthwise so that they can be inserted into a test tube. Push the folded filters to the bottom of the test tube with the applicator stick. Add to the test tube any particulate material remaining in the filter holder or collected on the weighing paper.

2. Pipette 5.0 mℓ of benzene into the test tube. This amount of solvent should completely cover the filters. Be careful during the subsequent extraction and filtering procedures to avoid significant loss of benzene by evaporation.

3. Place the test tubes in the test tube support in the ultrasonic bath so that the level of water in the bath is above the level of the solvent. Turn on the ultrasonic bath and sonicate the sample for 5 min.

4. Decant the solvent into an Allihn tube and collect the filtrate in a small vial. Force the solvent through the Allihn filter under positive nitrogen pressure. This may be accomplished by connecting the nitrogen cylinder to a glass "T," leaving one arm of the "T" open and connecting the other arm to a No. 4 one-hole rubber stopper, which is pressed against the top of the Allihn tube; pressure is controlled with a finger placed against the open arm of the "T." When the filtration has been completed, close the vial tightly with a Teflon-lined screw cap.

8.3.2 Gravimetric Determination

1. Transfer 1.0 mℓ of the benzene solution to a tared Teflon cup. Evaporate the solvent in a preheated vacuum oven at 40°C and 200 torr and continue drying for a total of 2 hr. The residue should be visibly dry in about 1 hr and in 2 hr all of the benzene will have been removed.

2. Equilibrate the sample for at least 30 min in a weighing room where the temperature and humidity are kept constant. Determine the weight of the residue to the nearest microgram. Because of the small weight difference being measured, it is critical that the temperature and humidity be the same when the residue is weighed as when the empty Teflon cup is weighed.

9. Calibration and Standards

No calibration or standards are required for this method.

10. Calculations

The result of this analysis is expressed as the weight (in mg) of benzene-soluble material in a filter sample. The weight of the residue from a 1.0-mℓ aliquot of sample extract is corrected by subtracting the average weight of the residue from aliquots of the blank-filter extracts. This corrected weight is multiplied by 5 to obtain the total amount of benzene-soluble material in the sample.

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THIOPHENE IN AIR

Measurements Research Branch

Analytical Method

Analyte:	Thiophene	**Method No.:**	P&CAM 255
Matrix:	Air	**Range:**	0.05 to > 7 mg/m³
Procedure:	Adsorption on charcoal, desorption with toluene, GC analysis	**Precision (CV):**	0.032 at 5 - 500 μg (Analytical)
Date Issued:	3/25/77	**Classification:**	E (Proposed)
Date Revised:			

1. **Principle of the Method**
   - 1.1 A known volume of air is drawn through a charcoal tube to trap the thiophene vapor present.
   - 1.2 The charcoal in the tube is transferred to a small air-tight sample container, and the analyte is desorbed with toluene.
   - 1.3 An aliquot of the desorbed sample is analyzed by gas chromatography using a sulfur flame photometric detector.
2. **Range and Sensitivity**
   - 2.1 The range of the sulfur detector for the quantitation of thiophene is dependent upon the type of detector and chromatograph used. For a flame photometric detector in a Tracor MT 220 Gas Chromatograph, the useful range for quantitation was 16 to 64 ng of thiophene per aliquot injected. This range corresponds to 3.2 to 12.8 μg of thiophene per sample solution obtained in the recovery from the charcoal.
   - 2.2 For a 70-liter air sample, this method is applicable to air concentrations ranging from 0.05 mg/m³ to levels above 7 mg/m³. The upper limit depends upon the capacity of the charcoal tube and dilution of the sample solution.

     At a detection limit of 4 ng per injection (0.8 μg per sample solution), it is estimated that thiophene at a concentration of 0.01 mg/m³ could be detected in a 70-liter air sample.
3. **Interferences**
   - 3.1 When the amount of water in the air is so great that condensation actually occurs in the charcoal tube, thiophene vapors may not be trapped efficiently.
   - 3.2 Any compound which has the same retention time compared to that of thiophene at the operating conditions described in this method may interfere with the analysis. Although the sulfur flame photometric detector has a high specificity for sulfur compounds, it will respond to other types of compounds, particularly those in high concentrations.
   - 3.3 When interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
4. **Precision and Accuracy**
   - 4.1 The coefficient of variation (CV) for the analytical method in the range 5 to 500 μg/charcoal tube sample is 0.032.
   - 4.2 The bias in the sampling and analytical method has not been determined.

4.3 The precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise because the pump is usually calibrated for one tube only.

5. **Advantages and Disadvantages of the Method**

5.1 The sampling device is small, portable, and involves no liquids.

5.2 A disadvantage of the method is that the capacity of the charcoal tube with respect to thiophene is limited. When the sample loading in the backup section of the tube exceeds 10% of that found in the front section, the possibility of sample loss exists.

5.3 Since the response of the sulfur flame photometric detector is proportional to the square of the quantity of thiophene, the quantitation range of thiophene is quite limited within one full scale deflection of the strip chart recorder. If the peaks are measured without the aid of an electronic integrator, solutions of thiophene in concentrations above this range must be diluted.

6. **Apparatus**

6.1 Personal sampling pump capable of maintaining a flow of air through the charcoal tube at a rate of 1 liter per min with an accuracy of ± 5%.

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop must be less than one inch of mercury at a flow rate of 1 liter per min.

6.3 Gas chromatograph equipped with a flame photometric detector specific for sulfur.

6.4 Column (1.8 m × 4 mm I.D.) constructed from borosilicate glass and packed with 3% OV-210 on 80/100 Gas Chrom Q. Other columns capable of performing the required separations also may be used.

6.5 Syringes, 10-μl.

6.6 Pipets, 1-ml.

6.7 Volumetric flasks, 10-ml and other convenient sizes for preparing standard solutions.

6.8 Glass vials, 2-ml.

6.9 Parafilm.

7. **Reagents**

7.1 Toluene, chromatographic quality.

7.2 Thiophene of known purity.

8. **Procedure**

8.1 **Cleaning of equipment.** All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 **Calibration of Personal Sampling Pumps.** Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume taken.

8.3 **Collection and Shipping of Samples**

8.3.1 Immediately before sampling, the ends of the tube should be broken to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a backup and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be vertical during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 Care should be taken to measure the flow rate, time and volume as accurately as possible. The sample should be taken at a flow rate of 1.0 liter per minute or less and should have a volume of no more than 70 liters.

8.3.6 The temperature, pressure, and relative humidity of the atmosphere being sampled should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 **Analysis of Samples**

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml glass vial. The separating section of foam is removed and discarded; the second section is transferred to another vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1 ml of toluene is pipetted into each vial containing the charcoal. Each vial is sealed. At least 1 hour should be allowed for desorption to be complete. During this time, each sample is agitated occasionally.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 40 ml/min nitrogen carrier gas flow
2. 150 ml/min hydrogen gas flow to the detector
3. 50 ml/min oxygen gas flow to the detector
4. 175°C inlet temperature
5. 190°C detector temperature
6. 50°C column temperature

8.4.4 By means of the solvent-flush injection technique, inject 5-μl aliquots of the sample solutions into the gas chromatograph. If a sample gives a peak which is larger than the largest peak, dilute an aliquot of the sample to bring the sample onto the calibration curve.

8.5 **Determination of Desorption Efficiency**

8.5.1 Activated charcoal equivalent to the amount in the front (larger) section of the sampling tube (100 mg) is poured into a 2-ml glass vial. This charcoal must be from the same batch as that used in obtaining the samples. A known amount of either neat thiophene or thiophene in toluene solution is applied directly onto the charcoal with a microliter syringe, and the vial is sealed with Parafilm.

8.5.2 Six samples are prepared in the above manner and allowed to stand overnight to assure complete adsorption of the thiophene onto the charcoal. A parallel blank vial should

be treated in the same manner except that no sample is added to it. The sample and blank vials are treated with toluene according to Section 8.4.2 to allow desorption to take place.

8.5.3 Six standards are prepared by adding the same quantity of thiophene used in preparing the samples to 1-ml portions of toluene.

8.5.4 The samples and standards are analyzed in pairs according to Section 8.4.

8.5.5 The blank is analyzed according to Section 8.4.

8.5.6 The desorption efficiency, DE, of each sample equals the difference between the square root of each sample peak height and the square root of the blank peak height divided by the square root of the corresponding standard peak height or

$$DE = \frac{\sqrt{\overline{H}} - \sqrt{\overline{H_b}}}{\sqrt{\overline{H_s}}}$$

where:

H = the peak height of the sample

H_b = the peak height of the blank

H_s = the peak height of the standard

The average DE is calculated from the six DE values obtained.

8.5.7 Since the desorption efficiency can vary with the quantity of thiophene adsorbed, the DE should be determined at different levels of thiophene. The values of DE obtained can be used to construct a plot of desorption efficiency versus quantity of thiophene measured.

9. Calibration and Standards

9.1 A series of standard solutions of thiophene in toluene should be prepared. The range of concentrations of interest depends upon the useful range of the detector and may be in the vicinity of 3 to 13 ng/μl. A plot of the square root of the peak height versus the quantity of thiophene injected should produce a straight line intercepting the origin.

9.2 To compensate for drift in detector response, a standard of concentration falling in the middle of the calibration curve is selected. This standard is analyzed alternately with the samples. The average detector response for the two standard peaks bracketing a sample thiophene peak, rather than the calibration curve, is used to calculate the quantity of thiophene in the sample.

10. Calculations

10.1 Determine the quantity of thiophene in the aliquot analyzed in the gas chromatograph.

10.1.1 Average the heights of the two standard peaks which are bracketing the sample peak.

10.1.2 Determine the quantity of thiophene, N (in nanograms), in the sample injected:

$$N = N_s \sqrt{\frac{H}{\overline{H_s}}}$$

where:

N_s = the quantity of thiophene in the standard.

H = the peak height of the sample.

$\overline{H_s}$ = the average peak height of the standard.

10.2 Determine the total quantity of thiophene, Q (in micrograms), which has been desorbed from the two sections of charcoal:

$$Q = \left(\frac{N \cdot S \cdot F}{V}\right)_A + \left(\frac{N \cdot S \cdot F}{V}\right)_B$$

where:

S = the volume of the solution of thiophene in toluene before any dilution (expressed in milliliters and is usually 1 ml).

F = the factor by which the thiophene solution is diluted; e.g., a 1-ml sample diluted to 10 ml reflects a dilution factor of 10. If the solution is not diluted, F = 1.

V = the volume of thiophene solution which is injected into the chromatograph for analysis (expressed in microliters and is usually 5 μl).

A = the thiophene in the front section of the charcoal tube.

B = the thiophene in the back section of the charcoal tube.

10.3 If thiophene was found in the blank, make the appropriate correction.

10.4 Determine the total quantity of thiophene, Q_T, in the air sample by dividing the quantity Q (Section 10.2) by the desorption efficiency.

10.5 Determine the concentration, C, of thiophene in air:

$$C = \frac{Q_T}{V}$$

where:

C = the concentration of thiophene in mg/m^3.

Q_T = the total quantity of thiophene in the air sample as determined in Section 10.4.

V = the volume of air in liters.

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15. Supplementary Notes

16. Abstract (Limit: 200 words) Industrial hygiene sampling and analytical procedures adapted to coal conversion facilities were described. These procedures were designed for potentially hazardous substances believed to be present in the coal conversion facilities. Due to cost constraints not all analytical procedures were carried out at each study site. Instead the toxic substances have been ranked according to hazard and available sampling and analytical procedures, and a judicious selection was made of substances to be sampled and analyzed. High flow pumps were used for personal monitoring of polynuclear aromatics (PNAs) and for particulate and trace metal sampling. Sampling equipment used for determining total particulates and trace metals was described. Noise exposure was also examined at this time, as were exposures to excessive heat and radiation. Specifics of the analytical processes used were given for the analysis of aromatic amines in air, aromatic alcohols in air, selected hydrocarbon vapors in air, total particulate matter in air, polynuclear aromatic hydrocarbons in air, airborne toxic gases, airborne trace metals, airborne thiophenes and airborne mercaptans.

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