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SAMPLING AND ANALYSIS OF GASES AND VAPORS

Michael A. Coffman, C.I.H.
and
Jaswant Singh, Ph.D., C.I.H.
Clayton Environmental Consultants, Inc.
Novi, Michigan

NIOSH Project Officer
P.G. Rentos, Ph.D.
Scientist Director

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This textual unit represents one of a series of new and revised materials prepared by acknowledged authorities, expressly for the fourth edition of *The Industrial Environment—its Evaluation and Control*. The document is currently in preparation and has been retitled, *Evaluation and Control of the Occupational Environment*, to make it more inclusive. Our intent in publishing the series in this form, well ahead of publication of the entire book, is to disseminate valuable, state-of-the-art information relative to the occupational environment as early as practicable, in order to realize the maximum benefit therefrom.

DISCLAIMER

The material in this publication was collected from recognized experts in various universities and research institutions in order to present as wide a range of information on the subject as possible; thus, the opinions and conclusions expressed are not necessarily those of the National Institute for Occupational Safety and Health.

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16. Abstract (Limit: 200 words) Techniques which were available to the industrial hygienist for evaluating exposures to gases and vapors in the work environment were described. The applications and limitations of several sampling media and techniques were presented. General sampling considerations discussed included sampling strategies, and operational limits of sampling and analysis. Sampling media for gases and vapors included solid sorbents, activated charcoal, silica gel, porous polymers, tenax, proapaks, chromosorbs, XAD resins, other solid sorbents, multistage air sampling tubes, liquid absorbers, passive samplers, and flexible plastic bags/partially evacuated rigid containers. Desorption of contaminants and collection efficiency of solid sorbents were also discussed. Analytical techniques considered include gas chromatography, flame ionization detector, nitrogen/phosphorus detector, flame photometric detector, electron capture detector, hall conductivity detector, thermal conductivity detector, photoionization detector, high performance liquid chromatography, gas chromatography/mass spectrometry, volumetric methods, and ion chromatography. Quality assurance was discussed.				
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Michael A. Coffman, C.I.H.

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Jaswant Singh, Ph.D., C.I.H.

Clayton Environmental Consultants, Inc.
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INTRODUCTION

This chapter introduces the techniques available to the industrial hygienist for evaluating exposures to gases and vapors in the work environment. Over the past decade, rapid improvements have occurred in sampling and analytical methods and in the commercial availability of new, efficient sampling media and real-time monitoring instruments. These advances have enhanced our ability to obtain reliable measurements of workplace exposures. Despite these advances, however, the industrial hygienist must recognize the limitations of the different techniques to ensure that the results are neither misinterpreted nor given undue credibility. In this chapter, we discuss the applications and limitations of a variety of sampling media and techniques.

When developing a particular sampling

strategy, the reader should review the specific sampling and analytical methods available for the contaminants of interest. Several organizations, including the National Institute for Occupational Safety and Health (NIOSH), the U.S. Occupational Safety and Health Administration (OSHA), Lewis Publishers, Inc., and the American Society for Testing and Materials (ASTM), have compiled and published collections of sampling and analytical methods for gases and vapors. Addresses of these organizations are provided in figure 1.

Some of these methods are summarized in figure 2. The industrial hygienist should carefully select the sampling and analytical methods most suitable for the specific application. If the sampling is performed to determine compliance with a specific OSHA standard, it may be preferable to use the OSHA method, if available.

NIOSH Manual of Analytical Methods, Third Edition
Centers for Disease Control
National Institute for Occupational Safety & Health
4676 Columbia Parkway
Cincinnati, Ohio 45226-1998

Methods of Air Sampling and Analysis
OSHA Analytical Methods Manual
Occupational Safety & Health Administration
Salt Lake City Analytical Laboratory
P.O. Box 15200
1781 South 300 West
Salt Lake City, Utah 84115

Annual Book of ASTM Standards
American Society for Testing and Materials
1916 Race Street
Philadelphia, Pennsylvania 19103-1187

Methods of Air Sampling and Analysis
Lewis Publishers, Inc.
Intersociety Committee
121 South Main Street
Chelsea, Michigan 48118

Figure 1. Available Publications on Sampling and Analytical Methods for Gases and Vapors.

Gas or Vapor	Sampling Medium	Analytical Method	Interferences	Method
Ammonia	Liquid sorbent badge containing 0.01 N H_2SO_4	Ion chromatography	Gases which produce an ammonium ion in H_2SO_4 solution	NIOSH 6701
Ammonia	Midget impinger containing 0.1 N H_2SO_4	Colorimetric, Nessler reagent	Ammonium salts	NIOSH P&CAM 205
Ammonia	Glass midget bubbler containing 10 ml of 0.1 N H_2SO_4	Ion-specific electrode	Volatile amines and metals which form strong complexes with ammonia	OSHA ID-164
Ammonia	37-mm MCE prefilter and H_2SO_4 -treated silica gel sorbent tubes	Ion-specific electrode	Volatile amines	NIOSH S347
Ammonia	Sorbent tube containing H_2SO_4 impregnated carbon beads	Ion chromatography	Ammonium salts, volatile amines	OSHA ID-188
Chlorinated Terphenyl (60% chlorine)	37-mm glass fiber filter	Gas chromatography	Other chlorinated terphenyls	NIOSH 5014
Chlorine	Glass midget bubbler containing 10 ml of 0.1% sulfamic acid solution	Ion-specific electrode	Strong oxidizing agents, iodate, bromine, cupric ion, manganese dioxide, silver, and mercuric ion	OSHA ID-101
Cyanides (Aerosols/Gases)	37-mm MCE filter and midget impinger containing 10 ml of 0.1 N NaOH	Ion-specific electrode	Insoluble silver salts such as Cl^- , Br^- , and I^- ; heavy metals; sulfide ion	OSHA ID-120
Cyanides (Aerosols/Gases)	37-mm MCE filter and midget bubbler containing 10 ml 0.1 N KOH	Ion-specific electrode	Sulfide, chloride, iodide, bromide, cadmium, zinc, silver, nickel, cuprous iron, mercury	NIOSH 7904
Formaldehyde	2-(benzylamino) ethanol coated Chromosorb 102 or XAD-2 sorbent tube	Gas chromatography, flame ionization detector	Phenol, acid mists	NIOSH 2502
Formaldehyde	37-mm 1 μ m PTE filter and two midget impingers containing 1% sodium bisulfite	Chromotropic acid/Colorimetric	Phenols, alcohols, olefins, aromatic hydrocarbons, cyclohexanone	NIOSH 3500
Formaldehyde	2-(hydroxymethyl) piperidine coated XAD-2 sorbent tube	Gas chromatography, nitrogen selective detector	Acetone	OSHA 52

Figure 2. OSHA and NIOSH Methods for the Collection and Analysis of Some Common Gases and Vapors (Sheet 1 of 3).

Gas or Vapor	Sampling Medium	Analytical Method	Interferences	Method
Formaldehyde	Midget fritted glass bubbler containing 10% aqueous methanol solution	Differential pulse polarography	Polyvinyl chloride (PVC)	OSHA ID-102
Formaldehyde	Midget bubbler containing 15 ml Girard reagent	Polarography	Other volatile aldehydes, such as acrolein, crotonaldehyde, benzaldehyde, PVC	NIOSH 3501
Hydrogen Chloride (Inorganic acids)	Silica gel sorbent tube	Ion chromatography	Chlorine	NIOSH 7903
Hydrogen Sulfide	Silver nitrate impregnated Whatman 4 filter	Differential pulse polarography	Other inorganic sulfides	OSHA ID-141
Hydrogen Sulfide	Sodium sulfate desiccant tube and molecular sieve sorbent tube	Gas chromatography, flame photometric detector	Humidity, sulfur-containing compounds	NIOSH P & CAM 296
MDI	Glass fiber filter impregnated with reagent	High pressure liquid chromatography	Light	NIOSH P & CAM 347
MDI	Midget impinger containing acid absorbing solution	Colorimetric	Aromatic amines, TDI	NIOSH P & CAM 142
MDI	Glass fiber filter coated with 1 mg 1-(2-pyridyl) piperazine	High pressure liquid chromatography	None	OSHA 47
Nitrogen Dioxide	Fritted bubbler containing Saltzman reagent	Colorimetric	Ozone, nitric oxide	NIOSH P & CAM 108
Nitrogen Dioxide	Triethanolamine (TEA)-impregnated molecular sieve sorbent tube	Colorimetric, Saltzman reagent	Inorganic nitrites	NIOSH P & CAM 231
Nitrogen Dioxide	Palmer tube with three TEA-treated screens	Visible absorption spectrophotometry	Particulates in dusty environments	NIOSH 6700
Nitrogen Dioxide	TEA-impregnated molecular sieve sorbent tube	Ion chromatography	Chloride ion	OSHA ID-182
Sulfur Dioxide	Midget bubbler containing 0.3 N potassium hydroxide	Titration with barium perchlorate	Volatile phosphates	NIOSH S308

Figure 2. OSHA and NIOSH Methods for the Collection and Analysis of Some Common Gases and Vapors (Sheet 2 of 3).

Gas or Vapor	Sampling Medium	Analytical Method	Interferences	Method
Sulfur Dioxide	37-mm MCE prefilter and midjet fritted glass bubbler containing 10 to 15 ml 0.3 N H ₂ O ₂	Ion chromatography	Other particulate, sulfate compounds	OSHA ID-104
Sulfur Dioxide	SKC Lot 125 impregnated charcoal sorbent tubes	Ion chromatography	Sulfate	OSHA ID-107
TDI	Glass fiber filters coated with 0.1 mg or 1 mg 1-(2-pyridyl) piperazine	High-pressure liquid chromatography	None	OSHA 42
TDI	Nitro reagent-coated glass wool sorbent tube	High-pressure liquid chromatography	None	NIOSH 2535

Figure 2. OSHA and NIOSH Methods for the Collection and Analysis of Some Common Gases and Vapors (Sheet 3 of 3).

An air contaminant is considered to be a gas if this is its normal physical state at room temperature (25°C) and one-atmosphere pressure (760 mm Hg). An example of a gas is chlorine (Cl₂). If, on the other hand, the substance is normally a liquid (or solid) under these conditions, then the gaseous component of the substance in equilibrium with its liquid (or solid) state is called a vapor. An example of a vapor is benzene (C₆H₆). The position of this equilibrium is indicated by the vapor pressure of the material. An estimate of the equilibrium concentration of the contaminant vapor can be obtained by dividing its vapor pressure by atmospheric pressure.

The industrial hygienist should consult with the analytical laboratory about the method of choice as an early part of survey planning. The laboratory can assist in choosing sampling and analytical methods which meet the sensitivity and specificity criteria appropriate to the environment being sampled. The laboratory can also help choose a sampling medium that is compatible with the analytical method selected.

GENERAL SAMPLING CONSIDERATIONS SAMPLING STRATEGIES

The discussion in this section only pertains to methods of sampling. There are a host of other considerations such as the number of workers to be sampled and sampling durations that enter into the proper design and implementation of a

sampling plan to monitor employee exposure. Such considerations are the subject of another chapter of this publication.

Two basic types of samples are collected to evaluate employee exposures: grab and integrated (Miller et al., 1975). Grab samples are collected to measure gas and vapor concentrations at a point in time and are used, therefore, to evaluate "peak" exposures for comparison to "ceiling" limits. The purpose of collecting grab samples is to evaluate contaminant sources or to measure contaminant levels from intermittent processes or other sources. Grab or instantaneous samples of an atmosphere to be analyzed for its gaseous components are collected using rigid containers, such as syringes or partially evacuated flasks or cans, or in nonrigid containers, such as gas bags.

Both integrated and instantaneous measurements of gases and vapors may also be performed using detector tubes or direct-reading instruments. Measurements of concentrations that may be immediately dangerous to life or health (IDLH) are best performed by using direct-reading instruments equipped with alarm systems. Alarms should be set to provide a suitable margin of safety. Most organic vapors and inorganic gases such as carbon monoxide, arsine, phosphine, hydrogen cyanide, and chlorine are typical of contaminants that can reach IDLH concentrations and are easily measured by direct-reading methods. These methods are described

in greater detail in the chapter on "Direct-Reading Instruments for Determining Concentrations of Aerosols, Gases, and Vapors."

Integrated sampling of the work environment must be performed when the composition of the air being sampled is nonuniform with respect to time and when compliance or noncompliance with an 8-hour time-weighted average (TWA) exposure limit must be established. Short-term integrated samples may be required to evaluate "peak" exposures when direct-reading instruments are not available or "grab" sampling methods are not practical. The decision regarding sampling duration and/or sample volume must take into consideration the purpose of sampling and the sensitivity of the analytical method. The quality of any industrial hygiene measurement depends on the accurate measurement of the mass of contaminant collected on the sampling medium and on the accurate measurement of the volume of air sampled.

Integrated sampling, covering the entire period of exposure, is required most often because airborne contaminant concentrations during a typical workshift vary considerably with time. Instantaneous measurements (grab samples) taken at any given period, therefore, do not reflect the average worker exposure for the shift. Most industrial hygiene measurements are carried out to determine the 8-hour TWA exposure and results are compared with the OSHA permissible exposure limit (PEL), or the threshold limit values (TLVs) of the American Conference of Governmental Industrial Hygienists (ACGIH), or other applicable limits or guidelines such as the NIOSH-recommended exposure limits. Integrated sampling is required even for determining compliance with short-term exposure limits (STEL) performed over a 15-minute period.

Integrated samples can be collected by bringing the gas or vapor into contact with a solid sorbent, water, or a chemical solution by passing air through a treated filter or by slowly filling an evacuated flask or a gas bag. The most commonly used integrated sampling method uses a sampling train comprised of a pump, a flow controller, a flow or volume measuring device, and the sampling medium. The first three components of the sampling train are generally incorporated into commercially available personal sampling pumps. While using such a sampling train, the accurate determination of sample volume is critical. Calibration of the sampling train (including the

collection medium) is therefore essential. (See the chapter on "Instruments and Techniques Used in Calibrating Air Sampling Equipment.")

Another commonly used method for collecting integrated samples is with passive samplers. This method is discussed in detail later in this chapter.

OPERATIONAL LIMITS OF SAMPLING AND ANALYSIS

In using any sampling technique, consideration must be given to the inherent limitations of the method, including sampler capacity, limit of detection (LOD), limit of quantitation (LOQ), and the upper useful limit of the calibration range (Eller, 1986 and Gunderson et al. 1980). In a given application, one or more of these factors will determine the minimum or maximum volume of air to be sampled and may determine the confidence which can be placed in the results.

The target concentration (C_t) is a preliminary estimate of the airborne concentration of the contaminant of concern. The target concentration may be estimated using previous sampling data (if available), through "range finding" with direct-reading instruments, detector tubes, or objectively, based on the experience of the industrial hygienist.

Sampler capacity (W_{max}) is a predetermined conservative estimate of the total mass of contaminant which can be collected on the sampling medium without loss or overloading. For gases and vapors, researchers at NIOSH have defined W_{max} as two-thirds of the breakthrough capacity of a solid sorbent. The breakthrough volume is defined as that volume of an atmosphere containing two times the PEL for the contaminant which can be sampled at the recommended flowrate before the efficiency of the sampler degrades to 95 percent.

The American Chemical Society (ACS) Committee on Environmental Analytical Chemistry defines the LOD as the amount of analyte which will give rise to a signal that is three times the standard deviation of the signal derived from the media blank. This corresponds to a relative uncertainty in the measurement of 100 percent at the 95 percent confidence level. The LOQ is the amount of analyte which will give rise to a signal that is 10 times the standard deviation of the signal from the media blank. This corresponds to a relative uncertainty in the measurement of

about 30 percent at the 95 percent confidence level.

The upper measurement limit (W_u) is the useful upper limit mg of analyte per sample) of the analytical instrument. The values of LOD, LOQ, and W_u for a given contaminant and analytical procedure should be obtained from the analytical laboratory before sampling.

The minimum sample volume for a quantitative determination (V_{min}) at the target concentration may be calculated as follows:

$$V_{min}(L) = \frac{LOQ (mg) \times 10^3 (L/m^3)}{C_t (mg/m^3)}$$

The maximum sample volume which may be collected with minimum risk of bias due to breakthrough or sampler overloading may be calculated as follows:

$$V_{max}(L) = \frac{W_{max} (mg) \times 10^3 (L/m^3)}{C_t (mg/m^3)}$$

The working range of a method is the range of contaminant concentration (mg/m^3) which may be quantitated at a specified air volume (liters). The lower boundary of the working range is defined by a sample that has a mass of contaminant equal to the LOQ. The upper boundary is defined by sampler capacity. Therefore, the working range may be calculated as follows:

$$\begin{aligned} \text{Lower Boundary (mg/m}^3\text{)} \\ = \frac{LOQ (mg) \times 10^3 (L/m^3)}{V (L)} \end{aligned}$$

$$\begin{aligned} \text{Upper Boundary (mg/m}^3\text{)} \\ = \frac{W_{max} (mg) \times 10^3 (L/m^3)}{V (L)} \end{aligned}$$

SAMPLING MEDIA FOR GASES AND VAPORS

SOLID SORBENTS

The most widely used sampling media for gases and vapors are solid sorbents that adsorb the contaminant onto the surface of a solid material. These solid sorbents consist of small granules or beads as shown in figure 3. To be effective, a sorbent should:

1. Trap and retain all or nearly all of the contaminant from an airstream;

2. Be amenable to desorption of the trapped contaminants from the sorbent;
3. Have sufficient capacity to retain a large enough amount of the contaminant to facilitate analysis without creating too large a pressure drop across the sampling media;
4. Not cause a chemical change of the contaminant except when the analytical method is based on derivitization of the contaminant;
5. Adsorb the contaminant of interest even in the presence of other contaminants, possibly in higher concentrations than the contaminant of interest (Melcher et al., 1987).

Commonly used solid sorbents are shown in figure 4.

DESORPTION OF CONTAMINANTS

A contaminant is desorbed either thermally or by solvent extraction. Desorption efficiency is defined by NIOSH (NIOSH, 1985) as the fraction of a known quantity of analyte recovered from a spiked solid sorbent media blank. Desorption efficiency should be determined for each lot of solid sorbent used for sampling in the concentration range of interest. Solvent desorption, the most commonly used technique, is specified by NIOSH for most industrial hygiene analyses. The most common desorption solvent is carbon disulfide because it has a high desorption efficiency for many organic compounds and produces minimum interference in gas chromatographic analysis using flame ionization detection.

In some cases, however, the recoveries are poor when using carbon disulfide. For example, higher desorption efficiencies can be attained with mixtures such as methanol and methylene chloride when analyzing for cellosolves®. For specific alcohols, better desorption efficiencies are obtained with a mixture of carbon disulfide and another alcohol.

Other desorption solvents commonly used include water (for desorption of methanol from silica gel), a mixture of water and acids (for desorption of amines), toluene (for desorption of formaldehyde from 2-(hydroxymethyl)piperidine treated XAD sorbent), and acetone (for desorption of furfuryl alcohol from Porapak Q) (NIOSH, 1981).

Thermal desorption works by driving the contaminant off the sorbent by subjecting it to

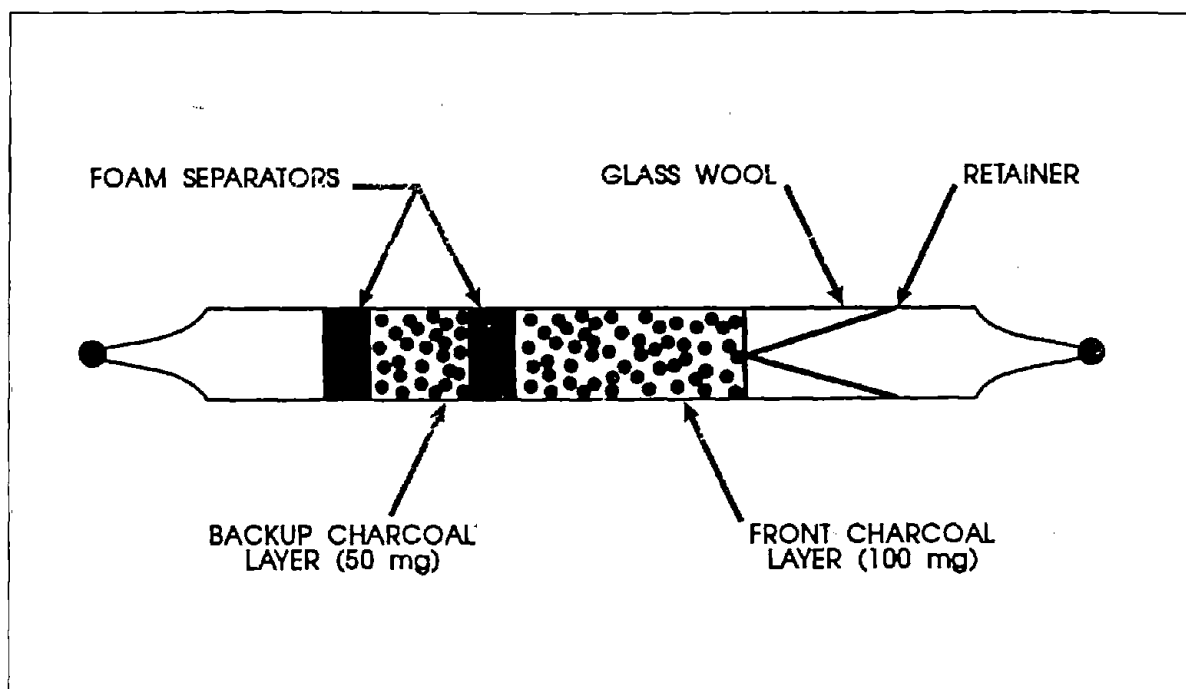


Figure 3. Activated Charcoal Sampling Tube.

a high temperature. The desorbed contaminant is carried in an inert gas stream (such as nitrogen, argon, or helium) directly into the analytical instrument (gaschromatograph [GC] or gas chromatography/mass spectrometry [GC/MS]). Because the contaminant is not diluted in a desorption solvent, and the entire mass of contaminant collected can be introduced directly into the analytical instrument (rather than an aliquot of a solution), this procedure yields very low limits, often subparts per billion, of detection. Additionally, thermal desorption is preferred in GC/MS analyses because solvent desorption may interfere with the analysis of volatile compounds by masking certain compounds.

ACTIVATED CHARCOAL. Charcoal is the most widely used solid sorbent for industrial hygiene sampling (Ballou, 1976 and Mueller and Miller, 1987). Many of the OSHA and NIOSH sampling procedures are based on sample collection on activated charcoal (NIOSH, 1981; NIOSH, 1985; and OSHA, 1985). Charcoal can be obtained from a variety of sources, including coconut shells, coal, wood, peat, and petroleum (Crisp, 1980). Each form has its own characteristics and uses. However, the most common forms are derived from either coconut shells or petroleum. Activated charcoal has a very high surface-area-to-weight ratio, which gives it high adsorptive

capacity. The high adsorptive capacity makes activated charcoal the ideal sorbent for chemically stable compounds which can be sampled on charcoal over a wide concentration range. High humidity has an adverse effect on the adsorptive capacity of charcoal (Saalwaechter, 1987). Charcoal is usually desorbed using a solvent such as carbon disulfide.

Gases such as hydrogen, nitrogen, oxygen, carbon monoxide, and methane with critical temperatures below -50°C and boiling points below -150°C cannot be collected efficiently on charcoal. In addition, low boiling compounds such as ammonia, ethylene, formaldehyde, hydrogen chloride, and hydrogen sulfide with critical temperatures below 150°C and boiling points below 0°C are *not* collected efficiently using charcoal (Crisp, 1980).

Charcoal has a highly reactive surface and, because of adsorbed oxygen, it presents a highly oxidizing surface (Guenier and Muller, 1984). Therefore, it cannot be used for the collection of reactive compounds such as mercaptans or aldehydes.

Activated carbon can be thermally desorbed at temperatures of 250°C or lower. At higher temperatures, adsorbed contaminants may decompose. In addition, offgassing of hydrocarbons from charcoal becomes a problem at higher

temperatures. High desorption temperatures are necessary in some cases for complete desorption.

SILICA GEL. Silica gel is chemically less reactive than charcoal (Guenier et al., 1986). In addition, because solvent desorption of polar compounds (such as methanol) from charcoal is inefficient, silica gel is a better collection medium for these compounds. A variety of silica gel sampling tubes are commercially available. Silica gel is the sorbent specified in the NIOSH methods for collecting organic amines, including aryl

(aromatic) amines such as aniline, anisidine, dimethyl aniline, monomethyl aniline, morpholine, p-nitroaniline, o-toluidine, and xyldines and alkyl amines such as butylamine, diethyl amine, ethyl amines, methyl amines, propylamines. Other contaminants which may be collected using silica gel include acetonitrile, methyl alcohol, and biphenyl ether. Using specifically prewashed silica gel tubes, NIOSH has developed sampling methods for acid gases. Because silica gel is hygroscopic, it shows a sharp decrease in capacity with increasing humidity.

Sorbent	Surface Area (m ²)	Pore Diameter (nm)	Temperature Limit (°C)	Composition	Desorption	Typical Applications
Activated Charcoal	—	—	250	Coconut shells or petroleum-based charcoal	Usually solvent CS ₂ is common	Broad range of organics
Tenax	25	—	400	Polymer of 2,6-diphenyl-p-phenylene oxide	Thermal	High boiling alcohols, diols, phenols, amines, diamines, ethanolamine, amides, aldehydes, ketones, methanol, acetonitrile, ethyl-methyl, ketose, benzene, styrene
Chromosorb 102	300 to 400	8.5	250	Copolymer of styrene and divinyl benzene	Thermal	Organic solvents, ketones, aldehydes, alcohols, glycols
Chromosorb 104	100 to 200	60 to 80	250	Copolymer of acrylonitrile and divinyl benzene	Thermal	Organic solvents, ketones, aldehydes, alcohols, glycols
XAD-2	300	9	200 to 250	Copolymer of styrene and divinyl benzene	Thermal	Organic solvents, ketones, aldehydes, alcohols, glycols
XAD-4	849	5	200 to 250	Copolymer of styrene and divinyl benzene	Thermal	Organophosphate pesticides
Silica Gel	100 to 200	0.3 to 2	—	Amorphous silica	Usually solvent	Methanol, benzidine, aldehydes, esters, amines, ketones, aromatic/compounds
Florisorb	298	—	500	Deactivated magnesium silicate	Usually solvent	PCBs

Figure 4. Properties of Some Typical Solid Sorbents.

POROUS POLYMERS. Porous polymers are a newer class of materials which are rapidly gaining acceptance in industrial hygiene sampling. Porous polymers have a lower surface-area-to-mass ratio and are much less reactive than charcoal. Their adsorptive capacity is therefore generally lower (Crisp, 1980). A principal advantage of Tenax® and some of the other porous polymers is their stability at elevated temperatures. This enables them to be thermally desorbed. The properties of the porous polymers are further described in figure 4.

The commercially available porous polymers include Tenax®, Porapak®, Chromosorbs® and XAD® resins (Adams et al., 1977 and Gallant et al., 1978).

Tenax. Tenax is a polymer of 2,6 diphenyl-p-phenylene oxide. It is the sorbent of choice when thermal desorption techniques are used. However, it has a relatively low surface area compared with XAD and Chromosorb resins. Tenax can be used to collect a broad range of organic compounds including high boiling alcohols, diols, phenols, amines, aldehydes, and ketones.

Porapaks. Porapaks comprise a group of porous polymers with a wide range of polarity. The least polar member of the group, Porapak P, has chromatographic properties that facilitate the separation of compounds such as ketones, aldehydes, alcohols, and glycols (Crisp, 1980). Porapak P is useful for the collection of dimethyl sulfide. At the other end of the spectrum, Porapak T is sufficiently polar to separate water and formaldehyde and is useful for the collection of hexachlorocyclopentadiene. Porapaks offer a range of sorbents, but the most polar members have disadvantages because of strong water retention and greater energy required to remove contaminants for analysis.

Chromosorbs. Chromosorbs have properties similar to those of the Porapaks. Chromosorb 101 is the least polar member. Chromosorb 104, the most polar, is noted for its water-retaining properties. Chromosorb 102 is particularly useful as a sorbent for air contaminants because of its large specific surface area and because a number of NIOSH methods specify this sorbent.

XAD Resins. These porous polymers include a number of different types. It should be noted

that XAD-2 is chemically equivalent to Chromosorb 102. Most applications of these materials as sorbents use XAD-2, but XAD-4 has been used to collect organophosphorus pesticides. XAD-7, 8, 9, and 12 are more suitable for polar compounds and XAD-1, 2, and 4 for nonpolar compounds.

OTHER SOLID SORBENTS. Other solid sorbents include molecular sieves, alumina, and polyurethane foam. The molecular sieves have limited applications, but form useful substrates for liquid media which are suitable for the collection of oxides of nitrogen (see figure 2). The use of alumina is also limited to special applications. Polyurethane foam is used primarily for collecting pesticides and polynuclear aromatic hydrocarbons (PAHs).

COLLECTION EFFICIENCY OF SOLID SORBENTS. Several factors may affect the collection efficiency of solid sorbents (Taylor et al., 1977):

Temperature. Because the adsorption process is exothermic, adsorption efficiency is limited at higher temperatures. In addition, reactivity increases with rising temperatures.

Humidity. As water vapor is adsorbed by a sorbent, its adsorption capacity for the contaminant of interest may decrease. This effect is most pronounced for sorbents such as charcoal.

Sampling Rate. Higher flowrates lower the sampling efficiency of solid sorbents. For sorbents whose capacity is significantly reduced by high humidity, reducing the sample flowrate may improve the collection efficiency.

Other Contaminants. The presence of significant concentrations of air contaminants (other than the contaminant of interest) may also reduce the collection efficiency of the sorbent for the target compound. This effect is most pronounced for contaminants within the same chemical family.

Sample Breakthrough. Most commercially available sampling tubes consist of two sections of sorbent separated by glass wool or polyurethane. In charcoal tubes, the second or backup section is usually one-third of the total weight of the charcoal. These two sections are desorbed and analyzed separately in the laboratory. As a general guideline, if

10 percent or less of the amount of contaminant collected on the front section is found on the backup section, significant loss of the compound (breakthrough) has probably not occurred. If greater than 10 percent is detected, breakthrough is evident and results should be reported as "breakthrough, possible sample loss." More specific information can be obtained by a detailed study of the breakthrough profiles for each specific sorbent and sorbate.

In some cases, a false indication of breakthrough may be caused by diffusion (migration) of the compounds collected on the front section to the backup section over an extended storage period. This equilibration approaches 33.3 percent on the backup section for the more volatile compounds. Sample migration can be reduced by refrigerating or freezing samples as soon as possible, or it can be eliminated by separating the front and backup sections.

MULTIPLE STAGE AIR SAMPLING TUBES.

In some situations, such as hazardous waste cleanup sites, industrial hygienists are called upon to evaluate employee or community exposures to complex mixtures of organic contaminants. The suitable sorbent for such applications is one that is capable of sampling a wide variety of contaminants with an analytical technique capable of both quantitative and qualitative analyses. Recently developed techniques use two-stage sampling tubes to adsorb organic contaminants followed by thermal desorption "cryogenic trapping" and analysis by GC/MS. One such technique, developed specifically for monitoring at hazardous waste sites, consists of two-stage glass sampling tubes (8-mm O.D. and 6-mm I.D., 25 cm long) which are flame-sealed at both ends and contain two sorbent sections retained by glass wool. The two sections include:

1. Front Section: 100 mg of Tenax-GC, 20/35 mesh
2. Back Section: 200 mg of Chromosorb 102, 20/40 mesh

By using a two-stage sorbent tube, the industrial hygienist is able to sample for a greater range of compounds than when using a sampling tube containing only a single sorbent (Singh et al., 1984).

Sorbent tubes are also used in combination with filter cassettes. For example, the NIOSH

method for sampling PAHs (NIOSH Method 5508) uses a PTFE (polytetrafluoroethylene) filter to collect the particulate fraction followed by an XAD-2 sorbent tube to collect vapors. Another example is measurement of organotin compounds (NIOSH Method 5504) using a glass fiber filter followed by XAD-2 sorbent tube.

LIQUID ABSORBERS

Sampling techniques that use liquid sampling media either include absorption based on solubility or may involve a reaction of the contaminant with the sampling solution. Four basic types of sampling devices have been used in conjunction with liquid absorbers: gas washing bottles, spiral and helical absorbers, fritted bubblers, and glass-bead columns. Of these, only the gas washing bottles and fritted bubblers are now used routinely (figure 5).

Gas Washing Bottles. Gas washing bottles include Drechsel types, standard Greenburg-Smith devices, and midjet impingers. The air is bubbled through the liquid absorber to secure intimate mixing of air and liquid, and the length of travel of the gas through the collecting medium is equivalent to the height of the absorbing liquid. These scrubbers are suitable for gases and vapors that are readily soluble in the adsorbing liquid or react with it. One unit or two units in series may be enough for efficient collection; however, in some cases, several in series may be needed to attain the efficiency of a single fritted glass bubbler. The advantages of these devices include simple construction; ease of rinsing; and, with the exception of Greenburg-Smith impingers, small liquid volume requirements.

Fritted Glass Bubblers. In fritted glass bubblers, air passes through formed porous glass plates and enters the liquid in the form of small bubbles. The size of the air bubbles depends on the liquid and the diameter of the orifices from which the bubbles emerge. Frits are classified as fine, coarse, or extra coarse, depending on the number of openings per unit area. The extra-coarse frit is used when a higher flow rate is desired. The heavier froth generated by some liquids increases the time of contact of gas and liquid. Fritted glass bubblers are more efficient collectors than the gas washing bottles and can be used for the majority of gases and vapors that are soluble in the reagent or react rapidly with it. Flow rates

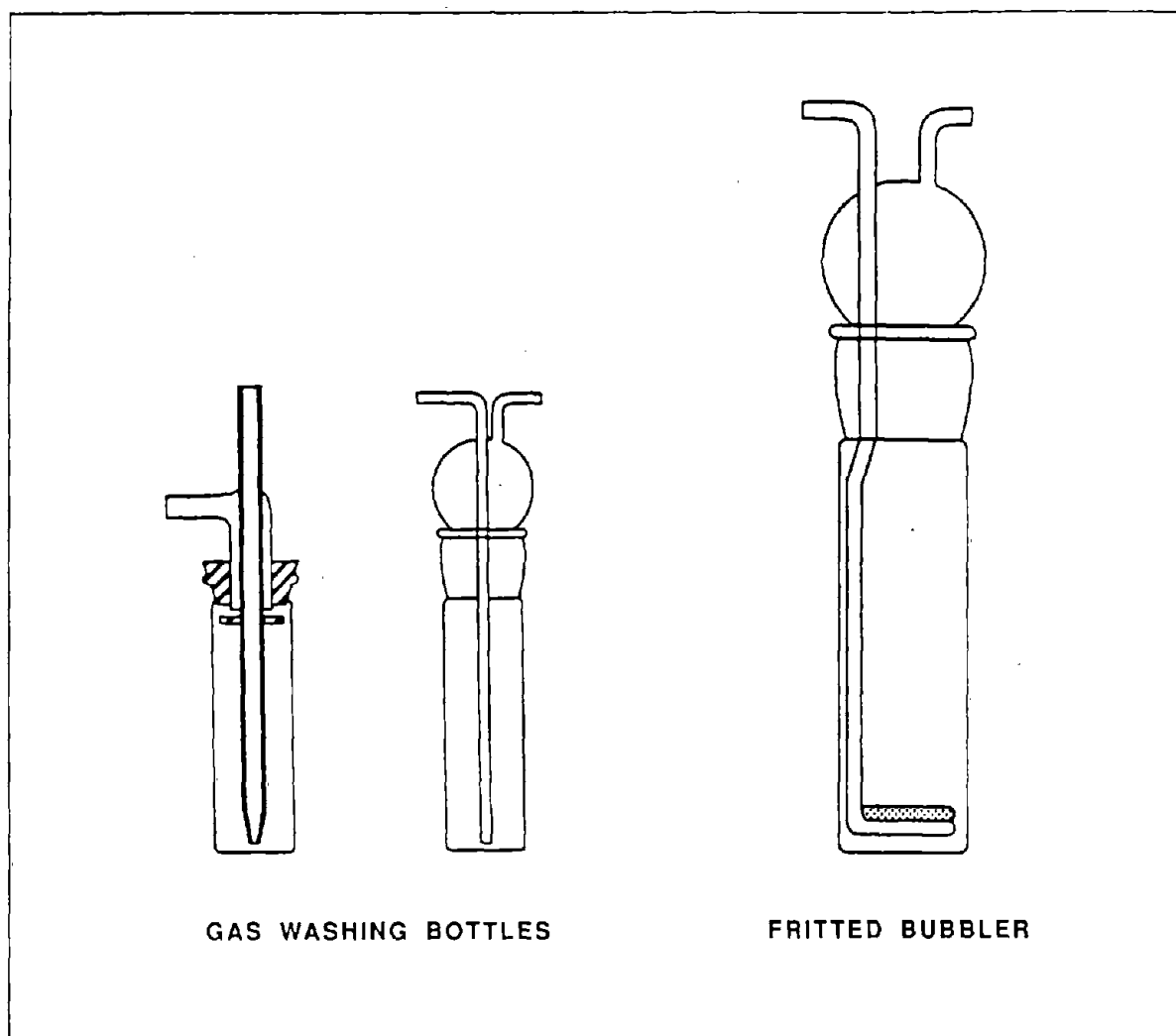


Figure 5. Absorbers: Simple Gas Washing and Fritted Bubbler.

between 0.5 and 1.0 liters per minute (l/min) are commonly used. Fritted glass is not suitable for sampling contaminants that form a precipitate during sampling which could clog the fritted glass or inhibit quantitative recovery of the sample. In this case, a gas washing bottle should be used. To prevent clogging, it may also be necessary to include a prefilter at the bubbler inlet when sampling air with a high particulate content.

Glass sampling devices are cumbersome, especially for "personal" sampling. Many liquid absorbers contain corrosive or toxic substances including strong acids or bases or toxic organics and pose safety and exposure problems for the users. In addition, the evaporation of the liquid

media poses problems of sample loss and worker exposure. Thus, the use of liquid absorbers has declined in favor of solid sorbent samplers.

PASSIVE SAMPLERS

Among the most important developments in air sampling technology in recent years is the development of passive sampling devices. Unlike conventional sampling devices which use a pump to move air through or past the sampling medium, passive samplers collect the contaminant through natural diffusion into the sampler and onto the collection medium. Passive samplers using either liquid absorbers or solid sorbents are commercially available (figure 6).

The monitors rely on a concentration gradient across a static or placid layer of air ("bound-

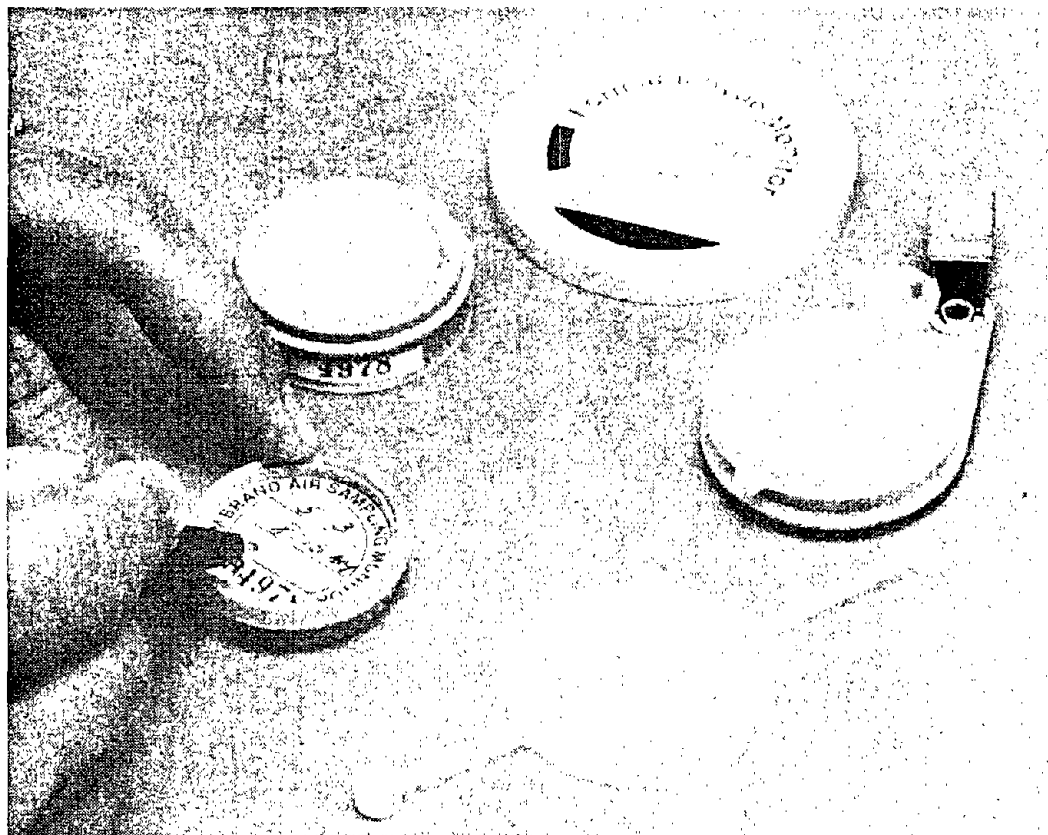


Figure 6. Passive Sampler.

ary layer") to induce a mass transfer (Soule, 1978 and 3M, 1983). The following equation, based on Fick's law, gives the steady-state relationship for the rate of mass transfer:

$$W = D(A/L) (C_1 - C_0)$$

Where W = Mass transfer rate

D = Diffusion coefficient

A = Frontal area of static layer

L = Linear depth of static layer

C_1 = Ambient vapor concentration

C_0 = Concentration at collection surface

By choosing an effective collection medium, so that C_0 remains essentially zero regardless of the value of C_1 , the mass transfer or collection rate is proportional to the ambient vapor concentration (C_1). It may also be noted that the units of $D(A/L)$ are volume per unit time, the same as for

the volumetric flow in a dynamic sampler. The uptake rate of the contaminant is approximately the product of $D(A/L)$ and C_1 .

Each gas or vapor being sampled has a specific diffusion coefficient (D). If a diffusion coefficient for the compound of interest has not been provided by the manufacturer, it must be determined experimentally or it may be estimated using several equations (Lugg, 1968). For environments with complex mixtures of contaminants, it may be difficult to establish an accurate diffusion coefficient (Hickey and Bishop, 1987). The accuracy and precision of the sampling process depends on the exposure time, the velocity and the orientation of the air stream moving past the sampler, and temperature effects (Harper and Purnell, 1987). The overall accuracy and precision of the reported concentration measurement are functions of the calibration standards, collection medium, and analytical method used. Of these factors, the potential ef-

fects of velocity and temperature distinguish passive samplers from conventional sampling techniques.

The thickness of the attached boundary layer on the outer surface of the monitor is a function of the velocity of air movement over the face of the monitor. Sampling that is independent of this air velocity can be achieved when the L term is large compared to the average boundary layer thickness.

Due to the relative ease and simplicity of sampling, passive sampling devices have become popular for routine sampling. Sampling can be conducted by relatively unskilled individuals. However, their use must be carefully evaluated by an experienced professional. When sampling out-of-doors or in complex environments, passive samplers may be prone to interferences and errors.

FLEXIBLE PLASTIC BAGS/PARTIALLY EVACUATED RIGID CONTAINERS

For some contaminants, grab samples may be collected in either flexible plastic bags or partially evacuated rigid containers or vessels (Conner and Nader, 1964, and Smith and Pierce, 1987). Examples of such contaminants include:

- Gases and highly volatile compounds for which adsorption methods are unsuitable due to the very low capacity of the sorbent or poor adsorption efficiency.
- Gases and vapors for which no alternative sampling technique is available.
- Reactive or unstable contaminants which must be analyzed immediately with portable, direct-reading instruments used onsite.

Commercially available sampling bags are listed in figure 7. The major drawbacks in the use of the flexible plastic bags are potential instability of the gas mixture in storage and sample loss through rupture or leakage in transport and handling. Loss of contaminant from a sampling bag may occur through reaction of the contaminant, adsorption of the contaminant onto the bag material, diffusion of the contaminant through the plastic, or leakage around the valve stem and seams. Despite these drawbacks, flexible plastic bags are widely used. To minimize errors, the following precautions should be taken before samples are collected:

1. Bags should be purged several times with an inert gas such as nitrogen to remove

TYPE	CHEMICAL COMPOSITION
5-layer aluminized	Inner layer-polyethylene
HALAR	Copolymer of ethylene and trifluoroethylene
SARAN	Polyvinylidene chloride
TEDLAR	Polyvinyl fluoride
TEFLON	FEP (fluorinated ethylene, propylene)

Figure 7: Commercially Available Gas Sampling Bags.

Adapted from: J.C. Posner and W.J. Woodfin: Sampling with Gas Bags 1: Losses of Analyte with Time, Applied Industrial Hygiene, Vol. 4, 1986.

any "trace" contaminants both before and between sampling periods.

2. Bags should be leak-tested using a soap solution applied to potential leakage points, such as valve stems and along seams, or by immersion of a filled bag in water.
3. Sampling bags selected should be relatively impermeable to the contaminant being sampled.
4. Bags should not be completely filled, especially if they will be transported by airplane. Changes in pressure or temperature can cause the bag to rupture.

Evacuated flasks include heavy-walled glass containers (figure 8) and other plastic or metal containers in which 99.97 percent or more of the air has been removed by a heavy-duty vacuum pump. Sampling is conducted by breaking the seal to permit the air to enter the flask. Commercially available evacuated flasks include glass bulbs and flasks provided by most laboratory supply houses.

ANALYTICAL TECHNIQUES

Perhaps the most significant and rapid advances in the industrial hygiene field are occurring in the analytical laboratory. Recent years have seen rapid automation in the industrial hygiene laboratory. Many wet-chemistry techniques have been replaced by instrumental methods, including ion chromatography. This is particularly true for inorganic ions which are in-

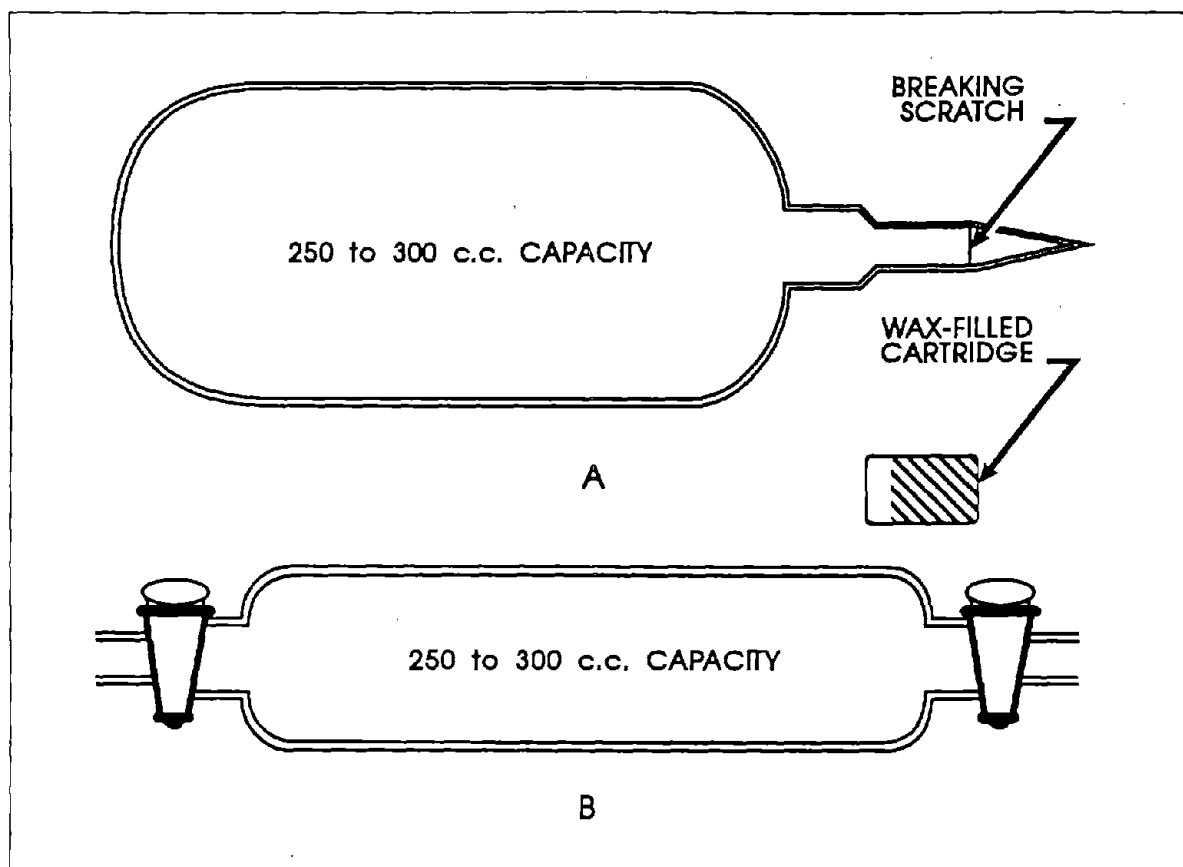


Figure 8. Grab Sample Bottles (A) Evacuated Flask, (B) Gas or Liquid Displacement Type.

Source: Sampling and Analysis of Mine Atmosphere, Miner's Circular 34, U.S. Dept. of Interior, 1948.

creasingly being analyzed by ion chromatographic techniques.

Chromatographic techniques, including gas chromatography, high performance liquid chromatography, gas chromatography/mass spectrometry, and ion chromatography, account for most of the procedures performed in today's industrial hygiene laboratory. Chromatography is the process of separating the components of a mixture by using a "mobile phase" to flush an aliquot of the sample through a "column."

If the mobile phase is a gas, the separation process is called "gas chromatography," and the mobile phase is usually called the "carrier gas." This technique is applicable to compounds that have sufficient vapor pressure and thermal stability to dissolve in the carrier gas and pass through the chromatographic column. The column may be heated to improve the analyte's solubility in the carrier gas. If the mobile phase is a liquid, the separation process is called "liquid chromatography." Liquid chromatography can be used to separate analytes that are at least

somewhat soluble in the solvent used for the mobile phase.

The chromatography column contains a "stationary phase," which may be a solid material that reversibly adsorbs the sample components, or it may be a liquid into which the sample components dissolve. Liquid stationary phases are held in place either by coating a thin film of a high viscosity liquid onto a porous "support" material or by chemically bonding the liquid stationary phase molecules to the support. The stationary phase polarity, chemical composition, surface area, and film thickness are some of the factors which influence the separation process.

After a sample is injected onto the head of a chromatography column, each chemical component in the sample repeatedly moves between being dissolved in the mobile phase and being held in or on the stationary phase. The stationary phase exhibits a different affinity for each component of the sample mixture. Chemical compounds which are more strongly attracted to the stationary phase take longer to be flushed

through the column by the mobile phase. The end result is that individual compounds elute from the column at different times.

A detector is used to measure the amount of each component as it elutes from the column. Because the response of the detector to a given compound is proportional to the amount of that material present, each component in a sample can be individually quantitated by comparing the detector response to the sample components with the detector response to standards containing known amounts of the compounds of interest. For accurate quantitation, the chromatographic column must separate or "resolve" the analyte from all other sample components to which the detector will respond.

The output signal of a chromatography detector is normally plotted against time. This plot is called a "chromatogram." The "baseline" is the part of the plot when the detector does not detect anything eluting from the column. A "peak" is a rise in the plot when one or more chemicals are detected as they elute from the column. The length of time between sample injection and the maximum point of a peak is called the "retention time." Electronic integration is commonly used to measure the size of a chromatographic peak.

GAS CHROMATOGRAPHY

Gas chromatography (GC) provides the industrial hygienist with a powerful tool for measuring low concentrations of organic vapors and gases. A wide variety of column stationary phases are available to optimize GC separations, and there is a selection of GC detectors available to optimize the sensitivity and selectivity of the analysis.

Samples for gas chromatographic analyses usually are organic vapors and gases collected on sorbents such as activated charcoal and silica gel. Common organic vapors determined by gas chromatography include acetone, benzene, methylene chloride, freons, toluene, xylenes, trichloroethane, and glycol ethers. Examples of other analyses often required in industrial hygiene surveys include hydrocarbon mixtures such as mineral spirits, VM&P naphtha, kerosene, and petroleum ether. Gas chromatography is also widely used in the determination of paint solvents, pesticides, polychlorinated biphenyls, and aliphatic and aromatic amines.

If the chromatographic column contains a stationary phase that is either a solid or a liquid

coated on a granular solid support "packing," the column is called a "packed column." If the stationary phase is coated on the inner wall of the column, it is called a "wall-coated open tubular" (WCOT) column. "Capillary columns" for gas chromatography have small inner diameters, usually ranging from 0.1 to 0.75 mm, while most packed GC column inner diameters are 2 mm or larger. Most capillary columns are WCOT columns because the absence of column packing reduces back pressure, allowing the use of longer, high resolution capillary columns. Capillary columns can improve the resolution of the analytes from interferences or, in some cases, allow a faster analysis, but they are more fragile and more complicated to use than packed columns.

Selection of the appropriate detector for the material of analytical interest is essential to realize the full potential of GC analysis. The following detection systems are most frequently used to maximize analytical sensitivity and selectivity:

Flame Ionization Detector (FID). This detector is quite sensitive to most organic compounds, including aliphatic and aromatic hydrocarbons, ketones, alcohols, ethers, and halogenated hydrocarbons. It is one of the most widely used gas chromatography detectors because it has good stability and a linear response over a wide concentration range.

The detector does not respond to carbon monoxide, carbon dioxide, hydrogen cyanide, formaldehyde, or formic acid, water, or most other inorganic compounds; it has little response to carbon disulfide. For this reason, carbon disulfide is frequently used as a charcoal tube desorption solvent for methods using a flame ionization detector.

In a flame ionization detector, the gas chromatograph column effluent is mixed with hydrogen, passes through a small opening or "jet," and is burned with an excess of air. Ionized combustion products are attracted to a metal "collector" around the flame, which is electrically charged at about +200 volts relative to the jet. Ions reaching the collector create an electrical current, which is amplified and recorded.

Nitrogen-Phosphorus Detector (NPD). This detector, also called a "thermionic" detector, is highly sensitive and selective for nitrogen and phosphorous compounds, including amines and organophosphates.

The detector is similar in principle to the flame ionization detector, except that ionization occurs on the surface of an alkali metal salt, such as cesium bromide, rubidium silicate, or potassium chloride. An older version of this detector, the alkali flame detector, uses a flame to heat the alkali metal salt. Newer detector designs electrically heat the alkali metal salt to improve stability and reduce response to hydrocarbon interferences.

Flame Photometric Detector (FPD). The flame photometric detector is used to measure phosphorus and sulfur containing compounds, such as sulfides and mercaptans.

The flame photometric detector measures phosphorus or sulfur containing compounds by burning the gas chromatograph column effluent in a hydrogen-air flame with an excess of hydrogen. Sulfur and phosphorus compounds emit light above the flame. A filter optimized to pass light at 393 nm is used to detect sulfur compounds, or a filter optimized to pass light at 535 nm is used to detect phosphorus compounds. A photomultiplier tube measures the amount of light after it has passed through the sulfur or phosphorus selective filter.

Electron Capture Detector (ECD). The electron capture detector is selective and highly sensitive for halogenated hydrocarbons such as polychlorinated biphenyls, halogenated insecticides and herbicides, nitrous oxide, and many other electron-capturing compounds. In an electron capture detector, a steady supply of electrons are emitted inside the detector and captured at a positively charged collector. Most electron capture detectors generate electrons using radioactive beta emitting isotopes, such as nickel 63 or tritium. When an electron-capturing compound is present in the gas chromatograph column effluent, fewer electrons reach the collector. The decrease in current is amplified and inverted so that the output signal from the detector increases as compounds are detected.

Hall Conductivity Detector (HCD). This detector is highly sensitive and selective for halogenated compounds and is frequently used for analyzing polychlorinated biphenyls. The Hall detector is more complicated than the electron capture detector and is not as sensitive for many halogenated analytes, but

it is less prone to interferences from nonhalogenated compounds. It also can be used in nitrogen or sulfur modes, although the thermionic and flame photometric detectors (respectively) are generally preferred for nitrogen and sulfur compounds.

When the Hall detector is used in the halogen mode, the column effluent is mixed with hydrogen and passes through an electrically-heated catalytic reactor tube. Halogenated compounds react to form strong inorganic acids (hydrofluoric, Hydrochlorine, Hydrobromide, Hydroiodide). The effluent from the reactor tube is transferred to a conductivity cell and mixed with a solvent, such as 1-propanol, which is pumped through the cell. The solvent inhibits dissociation except for strong inorganic acids. The difference in conductivity of the solvent before and after mixing with the reactor tube effluent is amplified and recorded.

Thermal Conductivity Detector (TCD). This is the most universal gas chromatography detector because it can measure most gases and vapors. It has low sensitivity compared to the other detectors. It is used primarily for analysis of low molecular weight gases such as carbon monoxide, carbon dioxide, nitrogen, and oxygen.

This detector measures the difference in thermal conductivity between the column effluent and a "reference" gas, which is taken from the same supply as the carrier gas. The column effluent and the reference gas pass through separate chambers in the detector which contain identical electrically-heated filaments. High molecular weight compounds present in the column effluent will conduct more heat away from the filament than the pure, low molecular weight reference gas, reducing the electrical resistance of the filament. The difference in resistance of the two filaments is amplified and recorded. The most common carrier gas for this detector is helium because it is inert and has a very low molecular weight.

Photoionization Detector (PID). This detector is sensitive to compounds with low ionization potentials that can be ionized by ultraviolet light. It can be used to selectively detect aromatics, alkenes, ketones, or amines in the presence of aliphatic chromatographic interferences. Only a small

fraction of the analyte molecules are actually ionized by the PID, so it can be used in series in front of another type of detector.

This detector is similar in principle to the flame ionization detector except that, instead of using a flame, it uses ultraviolet light to ionize the analyte molecules. Absorption of a photon by a molecule can cause the molecule to lose an electron if the energy of the photon is greater than the ionization potential of the molecule.

Different PID lamps are available to provide a selection of the energy level of the photons emitted. The lamp is chosen for selectivity of the analyte over the chromatographic interferences present in the sample.

For example, benzene has an ionization potential of 9.2 electron-volts (eV), and hexane has an ionization potential of 10.2 eV. A lamp which emits photons with an energy of 11 eV will ionize both, although it may be more sensitive to benzene. With a 10 eV lamp, the PID will measure only the benzene, even with a large amount of hexane present.

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

While gas chromatography is used to analyze the vast majority of airborne organic compounds, it is not suitable for compounds that have very high boiling points (low vapor pressures) and chemicals that may be unstable at elevated temperatures. For such chemicals, high performance liquid chromatography (HPLC) is the preferred technique. In contrast to gas chromatography where the analytes are carried through the column by a gas, liquid chromatography uses a liquid as the carrier or mobile phase. This removes the requirement that the contaminants be moderately volatile under the conditions of the experiment and replaces it with one which states that they simply be somewhat soluble. HPLC can be used with detectors, such as ultraviolet (UV) and fluorescence detectors, that can detect picogram quantities of toxic compounds such as herbicides, insecticides, quinones, and phthalates, and many carcinogenic compounds such as nitrosamines, polynuclear aromatics, and aflatoxins. HPLC has proven particularly valuable in the determination of PAHs, some of which are known or suspect carcinogens and many of which are ubiquitous to the environment.

Another major use of HPLC has been to

analyze for derivative airborne organic isocyanates (OSHA, 1985), both because it is more sensitive than the Mercuri colorimetric method and because it can separate the individual isocyanates (toluene-2,4-diisocyanate; toluene-2,6-diisocyanate; 1,6-hexamethylene diisocyanate; and methylene diphenyl isocyanate).

HPLC is suited for the analysis of bulk samples such as oils, tars, and resins. In combination with mass spectrometric techniques, it provides an effective quantitative as well as qualitative tool to the industrial hygiene chemist.

Suitable sampling media for subsequent HPLC analysis include glass fiber, silver membrane, cellulose ester membrane, and silica gel sorbent tubes. Impingers with liquid absorbents such as glycols are also suitable for HPLC analysis.

Two HPLC detectors are most frequently used for analyzing industrial hygiene samples:

1. The *ultraviolet absorbance detector* measures the absorbance of ultraviolet light by the HPLC column effluent. This detector is quite sensitive to aromatic hydrocarbons.

The basic components are an ultraviolet lamp, a flow-cell for the column effluent with a UV-transparent window, and a photodiode or other light measuring device. Some UV detectors can be operated at only one wavelength, typically 254 nm. Others can also operate at additional wavelengths by the use of fluorescent waveplates. A variable UV detector can be turned to any wavelength within its operating range.

2. The *fluorescence detector* measures the emission of light due to fluorescent chemicals eluting from the HPLC column. It is quite sensitive to highly conjugated aromatic compounds such as polynuclear aromatic hydrocarbons. Some analytical methods use derivatization reagents which make the analyte fluoresce.

A light source raises the fluorescent analyte to an unstable, higher energy level, which quickly decays in two or more steps, emitting light at longer wavelengths. The basic detector components are a lamp, a flow-cell for the column effluent with windows at a 90 degree angle, filters or diffraction gratings to select the "excitation" and "emission" wavelengths, and a photomultiplier tube or other light-measuring device.

Different fluorescence detector designs vary in versatility. Some use a collection of lamps, waveplates, and filters to provide a selection of excitation and emission wavelengths that may be more sensitive and selective for specific compounds. Other fluorescence detectors can be tuned to any wavelength within their range. Some automated models can rapidly change the wavelengths during chromatographic analysis to optimize the detector for different analytes from a single injection which elute at different retention times.

GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Gas chromatography/mass spectrometry (GC/MS) is a powerful analytical technique that uses a mass spectrometer as a gas chromatography detector. The column effluent from the gas chromatograph is ionized, the resulting ions are separated by their mass-to-charge ratio, and the abundance of the ions is measured and recorded. The basic parts of a mass spectrometer are the "source" where the sample is ionized, the "mass analyzer" which separates the ions by their mass, and the "ion-multiplier" which measures the amount of ions emerging from the mass analyzer.

The most common type of mass spectrometer ionization source produces ions by "electron impact." The column effluent from the gas chromatograph enters the mass spectrometer, the low-molecular weight carrier gas is removed, and the rest of the column effluent travels through a beam of electrons in a high vacuum. Some of the molecules are fragmented by the electron beam into numerous ions and neutral fragments. The fragmentation products are characteristic of the original molecule.

The positively charged ions then enter the mass analyzer, where rapidly changing electrical and magnetic radiation fields separate the ions according to their mass, sequentially allowing ions with each selected mass weight to pass through to the ion-multiplier. The ion-multiplier measures the amount of ions passing through the mass analyzer. Ions striking the ion-multiplier cause the emission of electrons, which are collected and amplified. A computer is used to store data pairs of the abundance of ions which the ion-multiplier is detecting and the mass weight of the ion which the analyzer is allowing to pass through to the ion-multiplier.

For each scan of the mass analyzer, the set of mass and abundance data pairs is called a "mass spectrum," typically displayed as a bar graph or a table, showing the abundance of positively charged ions at each mass weight. The mass spectrum pattern provides information about the structure of the original chemical compound and, in many cases, is sufficient to identify it.

Gas chromatographic/mass spectrometric techniques allow for both quantitative and qualitative determination of a variety of compounds that may not be detected or positively identified through gas chromatographic techniques alone. Some of the specific advantages and applications of GC/MS techniques are listed below:

1. Positive determination of environmental contaminants or confirmation of those detected by gas chromatography. Identification of complex mixtures. (Gas chromatography alone is not capable of positive identification.)
2. Analysis of complex mixtures of PAHs, which may be present in many industrial and community environments.
3. Determination of aromatic amines and nitrosamines. Nitrosamines are potent carcinogens and have been detected in foods, cigarette smoke, and many hydraulic and lubricating oils.
4. Identification of pyrolysis products from PCB fires.
5. Analysis of insecticides and herbicides. Conventional analytical methods frequently cannot resolve or identify the wide variety of industrial pesticides currently in use, but GC/MS can both identify and quantitate these compounds.
6. Analysis of products of pyrolysis or chemical decomposition such as those produced during heating of plastic materials and adhesives. Such information is often necessary for material safety data sheet (MSDS) preparation.

ION CHROMATOGRAPHY

Historically, methods for the analyses of anions have been generally complicated and prone to interferences. Recently, ion chromatography (which is a form of ion exchange chromatography) has become available to the industrial

hygiene chemist. It permits rapid and accurate analysis of samples

Some of the anions that are most suitable for ion chromatographic analyses include: sulfate, nitrate, phosphate, chromate, chloride, cyanamide, isocyanate, formate, sulfite, and thiocyanate. Ion chromatographic methods are also suitable for analyses of cationic species including ions of alkali and alkaline earth metals, inorganic ammonium salts, and salts of various amines. In addition, ion chromatography has proven useful in the analyses of carcinogens which can be determined as cations. These include aromatic amines such as b-naphthylamine, benzidine, hydrazines, aza arenes, and aziridines.

Major components of an ion chromatograph include a separation column, background ion suppressor column, various eluents, and a detector. The most commonly used detector for industrial hygiene work is the conductivity detector, which measures the electrical conductivity of the column effluent.

It is anticipated that ion chromatography will be used increasingly with the introduction of new types of columns, detectors, and derivatization methods.

VOLUMETRIC METHODS

In a volumetric method, the analysis is performed by measuring the volume of a solution of a known concentration required to react completely with the substance being determined. In the industrial hygiene analysis of gases and vapors, this generally means titrimetric methods which involve measuring the quantity of a reagent required to react completely with that substance. Detection of an endpoint is based upon the observation of some property of the solution that undergoes a characteristic change near the equivalence point. The commonly used properties to detect endpoint include changes in: color, turbidity, electric conductivity, electric potential, refractive index, and temperature of the solution.

For industrial hygiene purposes, titrimetric techniques have generally included determination of airborne concentrations of hydrogen chloride, nitric acid, caustic mist, sulfur dioxide, hydrogen sulfide, and ozone. More recently, these methods have largely been replaced by techniques more specific for the contaminant of interest, such as ion chromatography or instrumental colorimetric methods.

OPTICAL METHODS OF ANALYSIS

A common technique for many industrial hygiene analyses consists of the measurement of the absorption of light of a particular wavelength by a solution which contains the contaminant or a material which has been quantitatively derived from it. The process is termed absorption spectrophotometry or, if visible light is used, colorimetry. The extent to which light is absorbed by the solution is related to the concentration of the contaminant and the length of the solution through which the light beam passes by the Lambert-Beer law.

$$A = \log (I_{in}/I_{out}) = \log (1/T) = a \times b \times c$$

Where A = absorbance
 I_{in} = intensity of incident light beam
 I_{out} = intensity of beam leaving solution
 T = transmittance
 a = molar absorptivity constant
 b = path length
 c = concentration of absorbing material

Changes of color intensity have been the basis of many industrial hygiene analytical methods. For example, the use of Saltzman's reagent to determine the airborne concentration of nitrogen dioxide is a classic application of such methods. Although colorimetric techniques are still in use, they are rapidly being replaced by more sensitive instrumental methods such as ion chromatography.

Many of the optical analyses have been replaced by other methods. For example, methods of analysis for many organic compounds by ultraviolet (UV) spectrophotometry have been replaced by more convenient and sensitive methods, specifically gas chromatography. UV methods used in industrial hygiene analyses are now generally restricted to direct-measuring instruments, such as those used for measuring mercury vapors and real-time screening of organic compounds. Infrared spectrophotometric techniques are also commonly used in measuring airborne organic compounds. One advantage of the infrared technique is that it can be adapted to direct-reading instruments to measure a variety of gases and vapors. This is discussed further in the chapter on "Direct-Reading Instruments for Determining Concentrations of Aerosols, Gases, and Vapors."

For further information on analytical techniques the following are useful references:

1. *Instrumental Methods of Analysis: Seventh Edition*; H. Willard, L. Merritt, J. Dean, and F. Settle; Wadsworth Publishing Company, 1988.
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QUALITY ASSURANCE

Quality assurance is a vital component in the sampling and analysis of gases and vapors. Even the most sensitive and sophisticated analytical method is of little value unless supported by a rigorous quality assurance program. Erroneous results are extremely costly to the industrial hygienist because major decisions depend on these analyses.

Quality assurance programs required under the American Industrial Hygiene Association (AIHA) Laboratory Accreditation Programs are specific and detailed. The quality assurance program includes procedures in sampling and analysis. The quality assurance procedures in sampling involve calibration of field sampling equipment and a protocol for submitting field blanks to the laboratory. The major components of a Laboratory Quality Assurance Program are as follows:

1. Methods
2. Standards
3. Blanks
4. Blind samples
5. Recoveries
6. Replicate analyses
7. Interlaboratory/round-robin programs
8. Records
9. Instrument maintenance
10. Chain of custody

The laboratory's quality assurance program should be under the direct supervision of a quality assurance coordinator. If the size of the labora-

tory permits, this should be a full-time assignment. To minimize the conflict of interest between the laboratory's needs for rapid sample analyses and for reliable results, the quality assurance coordinator should report directly to upper management, rather than to a manager responsible for day-to-day laboratory operations.

Quality assurance in the industrial hygiene laboratory is described in greater detail in another chapter of this publication.

CALCULATIONS

The analytical laboratory usually determines the total amount of analyte collected on the sampling device. Convert this amount to the concentration of the analyte in the air sample by dividing by the volume of air which was sampled. The volume of air sampled is equal to the average sample collection flow rate times the length of time the sample was collected. Usually, the result needs to be calculated in units of mg/m^3 ; it may be necessary to first convert the air volume to cubic meters and the result to milligrams.

Many exposure standards for gases and vapors are expressed as the volume fraction of the analyte in the sample atmosphere, usually in units of parts per million (ppm). For example, many of the ACGIH TLVs are specified at a normal temperature and pressure (NTP) of 25°C (298°K) and 760 millimeters of mercury (mm Hg). This formula based on the ideal gas law, converts the measured analyte concentration from mg/m^3 to ppm at 25°C and 760 mm Hg:

$$\text{ppm} = \text{mg}/\text{m}^3 \times [24.45/\text{MW}] \times [(T + 273)/298] \times [760/P]$$

where:

mg/m^3 = analytical result, in units of milligrams per cubic meter

24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg

MW = molecular weight (grams/mole)

T = temperature ($^\circ\text{C}$) of air sampled

273 = conversion of $^\circ\text{C}$ to $^\circ\text{K}$

298 = normal temperature, in $^\circ\text{K}$

P = pressure (mm Hg) of air sampled

760 = normal pressure (mm Hg)

The conversion factors of 0.001 gm/mg , 0.001 m^3/liter , and 1,000,000 ppm cancel each other and are not shown in the equation.

The above formula is necessary for an accurate conversion from mg/m^3 to ppm when sampling at a high or low pressure, such as at a high altitude or at an extremely hot or cold

temperature. Otherwise, it is common practice among industrial hygienists to assume that sampling was conducted near NTP and to use this simplified version of the formula to convert the measured analyte concentration from mg/m^3 to ppm:

$$\text{ppm} = \text{mg}/\text{m}^3 \times 24.45/\text{MW}$$

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