

16

Ambient Air Sampling

I. ELEMENTS OF A SAMPLING SYSTEM

The principal requirement of a sampling system is to obtain a sample that is representative of the atmosphere at a particular place and time and that can be evaluated as a mass or volume concentration.¹ The sampling system should not alter the chemical or physical characteristics of the sample in an undesirable manner. The major components of most sampling systems are an inlet manifold, an air mover, a collection medium, and a flow measurement device.

The inlet manifold transports material from the ambient atmosphere to the collection medium or analytical device, preferably in an unaltered condition. The inlet opening may be designed for a specific purpose. All inlets for ambient sampling must be rainproof. Inlet manifolds are made out of glass, Teflon, stainless steel, or other inert materials and permit the remaining components of the system to be located at a distance from the sample manifold inlet. The air mover provides the force to create a vacuum or lower pressure at the end of the sampling system. In most instances, air movers are pumps.

¹ Real-time, remote monitoring systems, discussed in Chapter 18, do not require subsequent analysis.

The collection medium for a sampling system may be a liquid or solid sorbent for dissolving gases, a filter surface for collecting particles, or a chamber to contain an aliquot of air for analysis. The flow device measures the volume of air associated with the sampling system. Examples of flow devices are mass flow meters, rotameters, and critical orifices.

Sampling systems can take several forms and may not necessarily have all four components (Fig. 16.1). Figure 16.1(a) is typical of many extractive sampling techniques in practice, e.g. SO_2 in liquid sorbents and polynuclear aromatic hydrocarbons on solid sorbents. Figure 16.1(b) is used for "open-face" filter collection, in which the filter is directly exposed to the atmosphere being sampled. Figure 16.1(c) is an evacuated container used to collect an aliquot of air or gas to be transported to the laboratory for chemical analysis; e.g., polished stainless steel canisters are used to collect ambient hydrocarbons for air toxic analysis. Figure 16.1(d) is the basis for many of the automated continuous analyzers, which combine the sampling and analytical processes in one piece of equipment, e.g. continuous ambient air monitors for SO_2 , O_3 , and NO_x .

Regardless of the configuration or the specific material sampled, several characteristics are important for all ambient air sampling systems. These are collection efficiency, sample stability, recovery, minimal interference, and an understanding of the mechanism of collection. Ideally, the first three would be 100% and there would be no interference or change in the material when collected.

One example is sampling for SO_2 . Liquid sorbents for SO_2 depend on the solubility of SO_2 in the liquid collection medium. Certain liquids at the correct pH are capable of removing ambient concentrations of SO_2 with 100% efficiency until the characteristics of the solution are altered so that no more SO_2 may be dissolved in the volume of liquid provided. Under these circumstances, sampling is 100% efficient for a limited total mass of SO_2 transferred to the solution, and the technique is acceptable as long as sampling does not continue beyond the time that the sampling solution is saturated [1]. A second example is the use of solid sorbents such as Tenax for volatile hydrocarbons

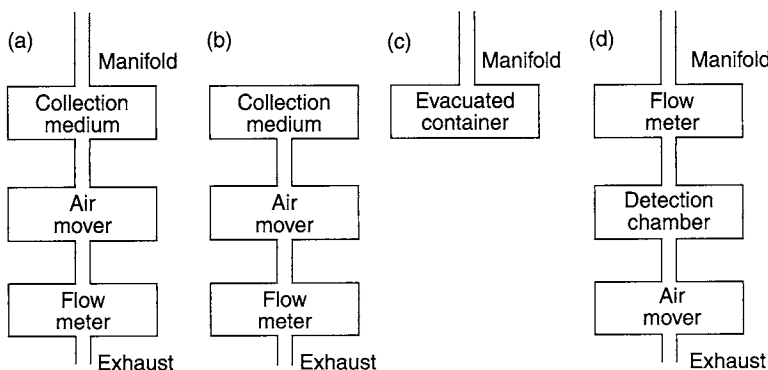


Fig. 16.1. Schematic diagram of various types of sampling systems.

by the physical adsorption of the individual hydrocarbon molecules on active sites of the sorbent [2]. Collection efficiency drops drastically when the active sites become saturated.

Sample stability becomes increasingly important as the time between sampling and analysis increases. Effects of temperature, trace contaminants, and chemical reactions can cause the collected species to be lost from the collection medium or to undergo a transformation that will prevent its recovery. Nearly 100% recovery is also required because a variable recovery rate will prevent quantification of the analysis. Interference should be minimal and, if present, well understood.

II. SAMPLING SYSTEMS FOR GASEOUS POLLUTANTS

Gaseous pollutants are generally collected by the sampling systems shown in Fig. 16.1(a)–(d). The sampling manifold's only function is to transport the gas from the manifold inlet to the collection medium in an unaltered state. The manifold must be made of nonreactive material. Tests of material for manifold construction can be made for specific gases to be sampled. In most cases, glass or Teflon will not adsorb or react with the gases. No condensation should be allowed to occur in the sampling manifold.

The volume of the manifold and the sampling flow rate determine the time required for the gas to move from the inlet to the collection medium. This residence time can be minimized to decrease the loss of reactive species in the manifold by keeping the manifold as short as possible.

The collection medium for gases can be liquid or solid sorbents, an evacuated flask, or a cryogenic trap. Liquid collection systems take the form of bubblers which are designed to maximize the gas–liquid interface. Each design is an attempt to optimize gas flow rate and collection efficiency. Higher flow rates permit shorter sampling times. However, excessive flow rates cause the collection efficiency to drop below 100%.

A. Extractive Sampling

When bubbler systems are used for collection, the gaseous species generally undergoes hydration or reaction with water to form anions or cations. For example, when SO_2 and NH_3 are absorbed in bubblers they form HSO_3^- and NHO_4^+ , and the analytical techniques for measurement actually detect these ions. Table 16.1 gives examples of gases which may be sampled with bubbler systems.

Bubblers are more often utilized for sampling programs that do not require a large number of samples or frequent sampling. The advantages of these types of sampling systems are low cost and portability. The disadvantages are the high degree of skill and careful handling needed to ensure quality results. Solid sorbents such as Tenax, XAD, and activated carbon (charcoal)

TABLE 16.1

Collection of Gases by Absorption

Gas	Sampler	Sorption medium	Air flow (L m ⁻¹)	Minimum sample (L)	Collection efficiency	Analysis	Interferences
Ammonia	Midget impinger	25 mL 0.1 N sulfuric acid	1-3	10		Nessler reagent	—
Benzene	Petri bubbler	10 mL of above	1-3	10	+95	Nessler reagent	—
	Glass bead column	5 mL nitrating acid	0.25	3-5	+95	Butanone method	Other aromatic hydrocarbons
Carbon dioxide	Fritted bubbler	10 mL 0.1 N barium hydroxide	1	10-15	60-80	Titration with 0.05 N oxalic acid	Other acids
Ethyl benzene	Fritted bubbler or midget impinger	15 mL spectrograde isooctane	1	20	+90	Alcohol extraction, ultraviolet analysis	Other aromatic hydrocarbons
Formaldehyde	Fritted bubbler	10 mL 1% sodium bisulfite	1-3	25	+95	Liberated sulfite titrated, 0.01 N iodine	Methyl ketones
Hydrochloric acid	Fritted bubbler	0.005 N sodium hydroxide	10	100	+95	Titration with 0.01 N silver nitrate	Other chlorides
Hydrogen sulfide	Midget impinger	15 mL 5% cadmium sulfate	1-2	20	+95	Add 0.05 N iodine, 6 N sulfuric acid, back-titrate 0.01 N sodium thiosulfate	Mercaptans, carbon disulfide, and organic sulfur compounds
Lead, tetraethyl, and tetramethyl	Dreschel-type scrubber	100 mL 0.1 M iodine monochloride in 0.3 N	1.8-2.9	50-75	100	Dithizone	Bismuth, thallium, and stannous tin
Mercury, diethyl, and dimethyl	Midget impinger	15 mL of above	1.9	50-75	91-95	Same as above	Same as above
	Midget impinger	10 mL 0.1 M iodine monochloride in .3 N hydrochloric acid	1-1.5	100	91-100	Dithizone	Copper
Nickel carbonyl	Midget impinger	15 mL 3% hydrochloric acid	2.8	50-90	+90	Complex with alpha-furil-dioxime	—

Nitrogen dioxide	Fritted bubbler (60–70 μm pore size)	20–30 mL Saltzman reagent ^a	0.4	Sample until color appears; probably 10 mL of air	94–99	Reacts with absorbing solution	Ozone in fivefold excess peroxyacyl nitrate
Ozone	Midget impinger	1% potassium iodide in 1 N potassium hydroxide	1	25	+95	Measures color of iodine liberated	Other oxidizing agents
Phosphine	Fritted bubbler	15 mL 0.5% silver diethyl dithiocarbamate in pyridine	0.5	5	86	Complexes with absorbing solution	Arsine, stibine, and hydrogen sulfide
Styrene	Fritted midget impinger	15 mL spectrograde isooctane	1	20	+90	Ultraviolet analysis	Other aromatic hydrocarbons
Sulfur dioxide	Midget impinger, fritted rubber	10 mL sodium tetrachloromercurate	2–3	2	99	Reaction of dichlorosulfite-mercurate and formaldehyde-pararosaniline	Nitrogen dioxide, ^b hydrogen sulfide ^c
Toluene diisocyanate	Midget impinger	15 mL Marcali solution	1	25	95	Diazotization and coupling reaction	Materials containing reactive hydrogen attached to oxygen (phenol); certain other diamines
Vinyl acetate	Fritted midget impinger and simple midget impinger in series	Toluene	1.5	15	+99 (84 with fritted bubbler only)	Gas chromatography	Other substances with same retention time on column

^a 5 g sulfanilic; 140 mL glacial acetic acid; 20 mL 0.1% aqueous *N*-(1-naphthyl) ethylene diamine.

^b Add sulfamic acid after sampling.

^c Filter or centrifuge any precipitate.

Source: Pagnotto, L. D., and Keenan, R. G., Sampling and analysis of gases and vapors, in *The Industrial Environment—Its Evaluation and Control*, pp. 167–179. US Department of Health, Education, and Welfare, US Government Printing Office, Washington, DC, 1973.

are used to sample hydrocarbon gases by trapping the species on the active sites of the surface of the sorbent. Figure 16.2 illustrates the loading of active sites with increasing sample time. It is critical that the breakthrough sampling volume, the amount of air passing through the tube that saturates its absorptive capacity, not be exceeded. The breakthrough volume is dependent on the concentration of the gas being sampled and the absorptive capacity of the sorbent. This means that the user must have an estimate of the upper limit of concentration for the gas being sampled.

Once the sample has been collected on the solid sorbent, the tube is sealed and transported to the analytical laboratory. To recover the sorbed gas, two techniques may be used. The tube may be heated while an inert gas is flowing through it. At a sufficiently high temperature, the absorbed molecules are desorbed and carried out of the tube with the inert gas stream. The gas stream may then be passed through a preconcentration trap for injection into a gas chromatograph for chemical analysis. The second technique is liquid extraction of the sorbent and subsequent liquid chromatography. Sometimes a derivatization step is necessary to convert the collected material chemically into compounds which will pass through the column more easily, e.g. conversion of carboxylic acids to methyl esters. Solid sorbents have increased our ability to measure hydrocarbon species under a variety of field conditions. However, this technique requires great skill and sophisticated equipment to obtain accurate results. Care must be taken to minimize problems of contamination of the collection medium, sample instability on the sorbent, and incomplete recovery of the sorbed gases.

Special techniques are employed to sample for gases and particulate matter simultaneously [3]. Sampling systems have been developed which permit the removal of gas-phase molecules from a moving airstream by diffusion to a coated surface and permit the passage of particulate matter downstream

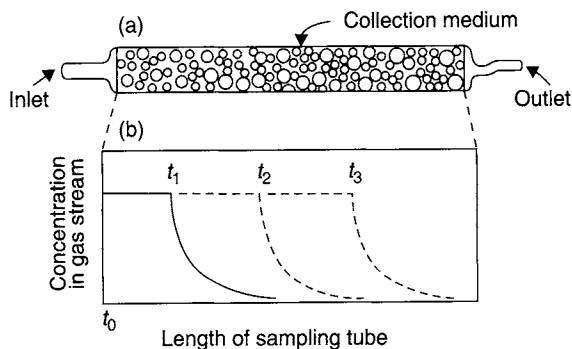


Fig. 16.2. Solid sorbent collection tube. (a) The tube is packed with a granular medium. (b) As the hydrocarbon-containing air is passed through the collection tube at t_1 , t_2 , and t_3 , the collection medium becomes saturated at increasing lengths along the tube.

for collection on a filter or other medium. These diffusion denuders are used to sample for SO₂ or acid gases in the presence of particulate matter. This type of sampling has been developed to minimize the interference of gases in particulate sampling and vice versa.

The third technique, shown in Fig. 16.1(c), involves collection of an aliquot of air in its gaseous state for transport back to the analytical laboratory. Use of a preevacuated flask permits the collection of a gas sample in a specially polished stainless steel container. By use of pressure–volume relationships, it is possible to remove a known volume from the tank for subsequent chemical analysis. Another means of collecting gaseous samples is the collapsible bag. Bags made of polymer films can be used for collection and transport of samples. The air may be pumped into the bag by an inert pump such as one using flexible metal bellows, or the air may be sucked into the bag by placing the bag in an airtight container which is then evacuated. This forces the bag to expand, drawing in the ambient air sample.

B. *In Situ* Sampling and Analysis

The fourth sampling technique involves a combination of sampling and analysis. The analytical technique is incorporated in a continuous monitoring instrument placed at the sampling location. Most often, the monitoring equipment is located inside a shelter such as a trailer or a small building, with the ambient air drawn to the monitor through a sampling manifold. The monitor then extracts a small fraction of air from the manifold for analysis by an automated technique, which may be continuous or discrete. Instrument manufacturers have developed automated *in situ* monitors for several air pollutants, including SO₂, NO, NO₂, O₃, and CO.

This approach is also improving for organic pollutants. For example, real-time gas chromatograph–mass spectrometers and open Pater Fourier.

III. SAMPLING SYSTEMS FOR PARTICULATE POLLUTANTS

Sampling for particles in the atmosphere involves a different set of parameters from those used for gases. Particles are inherently larger than the molecules of N₂ and O₂ in the surrounding air and therefore behave differently with increasing diameter. When one is sampling for particulate matter in the atmosphere, three types of information are of interest: the mass concentration, size, and chemical composition of the particles. Particle size is important in determining adverse effects and atmospheric removal processes. The US Environmental Protection Agency has specified a PM_{2.5} sampling method for compliance monitoring for the National Ambient Air Quality Standards (NAAQS) for particulate matter. This technique must be able to sample particulate matter with an aerodynamic diameter less than 10 μm with a prescribed efficiency.

Particles in the atmosphere come from different sources, e.g. combustion, windblown dust, and gas-to-particle conversion processes (see Chapter 10). Figure 2.2 illustrates the wide range of particle diameters potentially present in the ambient atmosphere. A typical size distribution of ambient particles is shown in Fig. 2.3. The distribution of number, surface, and mass can occur over different diameters for the same aerosol. Variation in chemical composition as a function of particle diameter has also been observed, as shown in Table 8.5.

The major purpose of ambient particulate sampling is to obtain mass concentration and chemical composition data, preferably as a function of particle diameter. This information is valuable for a variety of problems: effects on human health, identification of particulate matter sources, understanding of atmospheric haze, and particle removal processes.

The primary approach is to separate the particles from a known volume of air and subject them to weight determination and chemical analysis. The principal methods for extracting particles from an airstream are filtration and impaction. All sampling techniques must be concerned with the behavior of particles in a moving airstream. The difference between sampling for gases and sampling for particles begins at the inlet of the sampling manifold and is due to the discrete mass associated with individual particles.

A. Behavior of Particles at Sampling Inlets

Sampling errors may occur at the inlet, and particles may be lost in the sampling manifold while being transported to the collection surface. Figure 16.3 illustrates the flow patterns around a sampling inlet in a uniform flow field.

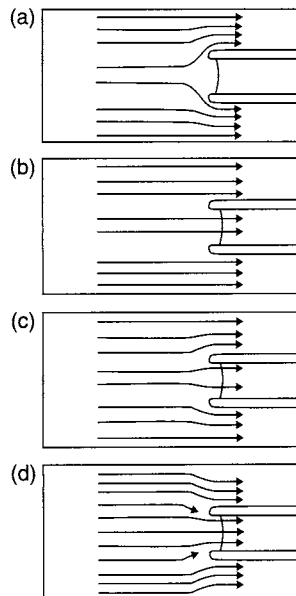


Fig. 16.3. The streamline flow patterns around a sampling inlet in a uniform flow field.

field. Figure 16.3(a) shows that when no air is permitted to flow into the inlet, the streamline flow moves around the edges of the inlet. As the flow rate through the inlet increases, more and more of the streamlines are attracted to the inlet. Figure 16.3(b) is called the *isokinetic condition*, in which the sampling flow rate is equal to the flow field rate. An example is an inlet with its opening into the wind pulling air at the wind speed. When one is sampling for gases, this is not a serious constraint because the composition of the gas will be the same under all inlet flow rates; i.e., there is no fractionation of the air sample by different gaseous molecules.

Transform infrared, differential optical absorption spectroscopy, and tuned lasers are being used with much success.

Particle-containing air streams present a different situation. Figure 16.3(b), the isokinetic case, is the ideal case. The ideal sample inlet would always face into the wind and sample at the same rate as the instantaneous wind velocity (an impossibility). Under isokinetic sampling conditions, parallel air streams flow into the sample inlet, carrying with them particles of all diameters capable of being carried by the stream flow. When the sampling rate is lower than the flow field (Fig. 16.3(c)), the streamlines start to diverge around the edges of the inlet and the larger particles with more inertia are unable to follow the streamlines and are captured by the sampling inlet. The opposite happens when the sampling rate is higher than the flow field. The inlet captures more streamlines, but the larger particles near the edges of the inlet may be unable to follow the streamline flow and escape collection by the inlet. The inlet may be designed for particle size fractionation; e.g., a $PM_{2.5}$ inlet will exclude particles larger than $2.5\mu\text{m}$ aerodynamic diameter (see Fig. 2.4).

These inertial effects become less important for particles with diameters less than $5\mu\text{m}$ and for low wind velocities, but for samplers attempting to collect particles above $5\mu\text{m}$, the inlet design and flow rates become important parameters. In addition, the wind speed has a much greater impact on sampling errors associated with particles more than $5\mu\text{m}$ in diameter [4].

After the great effort taken to get a representative sample into the sampling manifold inlet, care must be taken to move the particles to the collection medium in an unaltered form. Potential problems arise from too long or too twisted manifold systems. Gravitational settling in the manifold will remove a fraction of the very large particles. Larger particles are also subject to loss by impaction on walls at bends in a manifold. Particles may also be subject to electrostatic forces which will cause them to migrate to the walls of nonconducting manifolds. Other problems include condensation or agglomeration during transit time in the manifold. These constraints require sampling manifolds for particles to be as short and have as few bends as possible.

The collection technique involves the removal of particles from the air stream. The two principal methods are filtration and impaction. Filtration consists of collecting particles on a filter surface by three processes: direct interception, inertial impaction, and diffusion [5]. Filtration attempts to remove a very high percentage of the mass and number of particles by these

three processes. Any size classification is done by a preclassifier, such as an impactor, before the particle stream reaches the surface of the filter.

IV. PASSIVE SAMPLING SYSTEMS

Passive (or static) *sampling systems* are defined as those that do not have an active air-moving component, such as the pump, to pull a sample to the collection medium. This type of sampling system has been used for over 100 years. Examples include the lead peroxide candle used to detect the presence of SO₂ in the atmosphere and the dustfall bucket and trays or slides coated with a viscous material used to detect particulate matter. This type of system suffers from inability to quantify the amount of pollutant present over a short period of time, i.e., less than 1 week. The potentially desirable characteristics of a static sampling system have led to further developments in this type of technology to provide quantitative information on pollutant concentrations over a fixed period of time. Static sampling systems have been developed for use in the occupational environment and are also used to measure the exposure levels in the general community, e.g., radon gas in residences.

The advantages of static sampling systems are their portability, convenience, reliability, and low cost. The systems are lightweight and can be attached directly to individuals. Nonstatic sampling systems can, of course, also be attached to individuals, but are less convenient because the person must carry a battery-powered pump and its batteries. Static sampling systems are very reliable, and the materials used limit the costs to acceptable levels.

Two principles are utilized in the design of static samplers: diffusion and permeation [6,7]. Samplers based on the diffusion principle depend on the molecular interactions of N₂, O₂, and trace pollutant gases. If a concentration gradient can be established for the trace pollutant gas, under certain conditions the movement of the gas will be proportional to the concentration gradient (Fick's law of diffusion), and a sampler can be designed to take advantage of this technique. Figure 16.4 illustrates this principle. The sampler has a well-defined inlet, generally with a cylindrical shape, through which the pollutant gas must diffuse. At the end of the tube, a collection medium removes the pollutant gas for subsequent analysis and maintains a concentration gradient between the inlet of the tube and the collection medium. The mathematical relationship (Fick's law) describing this type of passive sampler is given by

$$R = -DA \left(\frac{dC}{dx} \right) \quad (16.1)$$

where R is the rate of transport by diffusion in moles per second, D is the diffusion coefficient in square centimeters per second, A is the cross-sectional area of the diffusion path in square centimeters, C is the concentration of species in moles per cubic centimeter, and x is the path length in centimeters.

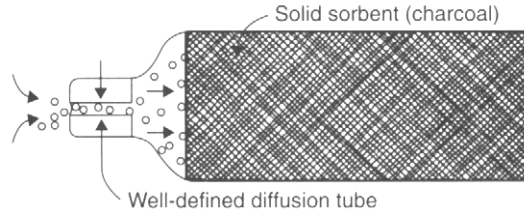


Fig. 16.4. Static sampler based on the diffusion principle.

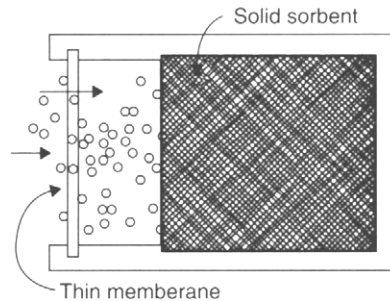


Fig. 16.5. Static sampler based on the permeation principle.

The ability of gases to permeate through various polymers at a fixed rate depending on a concentration gradient has been used to create static samplers. This principle was originally developed to provide a standard calibration source of trace gas by putting that gas in a polymer tube under pressure and letting the material diffuse or permeate through the wall to the open atmosphere. Permeation samplers operate in the reverse direction. Figure 16.5 illustrates this type of system. A thin film membrane is open to the atmosphere on one side and to a collection medium on the other. A pollutant gas in the atmosphere diffuses through the membrane and is collected in the medium. The mathematical relationship for a permeation sampler is given by

$$k = \frac{Ct}{m} \quad (16.2)$$

where k is the permeation constant, C is the concentration of gas in parts per million, t is the time of exposure, and m is the amount of gas absorbed in micrograms.

Permeation systems can be calibrated in the laboratory and then used in the field for sample collection for a fixed period of time, e.g., 8 h or 7 days. The sampler is returned to the laboratory for analysis. These systems can be made for specific compounds by selecting the appropriate collection medium and the polymer membrane (Table 16.2).

TABLE 16.2

Permeation Samplers for Selected Gases

Gas	Membrane	Sorber	Sensitivity
Chlorine	Dimethyl silicone (DMS) (single-backed)	Buffered (pH 7) fluorescein, 0.005% NaBr (0.31%)	0.013 ppm (8-h exposure)
Sulfur dioxide	DMS (single-backed)	Tetrachloromercurate (II)	0.01 ppm (8-h exposure)
Vinyl chloride	DMS (single-backed)	Activated charcoal (CS ₂ desorption)	0.02 ppm (linear to 50 ppm +)
Alkyl lead	DMS (unbacked)	Silica gel (ICI desorption)	0.2 µg
Benzene	Silicon polycarbonate	Activated charcoal (CS ₂ desorption)	0.02 ppm (8-h exposure)
Ammonia	Vinyl silicone	0.6% boric acid	0.4 ppm (8-h exposure)
Hydrogen sulfide	DMS (single-backed)	0.02 N NaOH, 0.003 M EDTA	0.01 ppm
Hydrogen cyanide	DMS (single-backed)	0.01 N NaOH	0.01 ppm (8-h exposure)

Source: West, P. W., *Am. Lab.* 12, 35-39 (1980).

V. SAMPLER SITING REQUIREMENTS

Sampling site selection is dependent on the purpose or use of the results of the monitoring program. Sampling activities are typically undertaken to determine the ambient air quality for compliance with air quality standards, for evaluation of the impact of a new air pollution source during the preconstruction phase, for hazard evaluation associated with accidental spills of chemicals, for human exposure monitoring, and for research on atmospheric chemical and physical processes. The results of ambient air monitoring can be used to judge the effectiveness of the air quality management approach to air pollution problems. The fundamental reason for controlling air pollution sources is to limit the buildup of contaminants in the atmosphere so that adverse effects are not observed. This suggests that sampling sites should be selected to measure pollutant levels close to or representative of exposed populations of people, plants, trees, materials, structures, etc. Generally, sites in air quality networks are near ground level, typically 3 m aboveground, and are located so as not to be unduly dominated by a nearby source such as a roadway. Sampling sites require electrical power and adequate protection (which may be as simple as a fence). A shelter, such as a small building, may be necessary. Permanent sites require adequate heating and air conditioning to provide a stable operating environment for the sampling and monitoring equipment.

VI. SAMPLING FOR AIR TOXICS

Public awareness of the release of chemicals into the atmosphere has gone beyond the primary ambient pollutants (e.g. SO₂ or O₃) and governments require air toxics management plans. One component of this process is the characterization of the air quality via sampling.

Most of the airborne chemicals classified as "air toxics" are organic compounds with physical and chemical properties ranging from those similar to formaldehyde found in the gas phase to polycyclic aromatic hydrocarbons (PAHs) which may be absorbed on particle surfaces. Air toxics also include a number of metals and their compounds. This range of volatility and reactivity represented by air toxics requires a variety of sampling techniques—from grab sampling to filter techniques followed by extraction and detailed derivatization techniques. When these compounds are present in the atmosphere, the concentration level can be quite low, in the parts per billion (ppb) to sub-ppb range for gases and the picogram per cubic meter range for particulate components. Two concentrations must be calculated for particle-bound contaminants: the concentrations of particles in the atmosphere (mass of particles per volume of air) and the concentration of contaminants sorbed to the particle (mass of each chemical per mass of particles). This generally requires extended sampling times and very sensitive analytical techniques for laboratory analysis.

The US Environmental Protection Agency established a pilot Toxics Air Monitoring System network for sampling ambient volatile organic compounds (VOCs) at ppb levels in Boston, Chicago, and Houston for a 2-year period [8]. Evacuated stainless steel canisters were used to collect air at 3 cm³ min for 24 h. The canisters were returned to a central laboratory and analyzed by cryogenic concentration of the VOCs, separation by gas chromatography, and mass-selective detection. This system provided information on 13 VOCs in three classes: chlorofluorocarbons, aromatics, and chlorinated alkanes.

A second sampling program in Southern California sampled for polychlorinated dioxins and polychlorinated dibenzofurans at seven locations [9]. Because of the semivolatile nature of these compounds, a tandem sampler was used with a glass fiber filter to collect the particulate-associated components followed by a polyurethane foam sorbent trap to collect the vapor-phase portion. These samples were returned to the laboratory, where they were extracted and analyzed with high-resolution gas chromatography and high-resolution mass spectrometry. The observed concentrations were in the picogram per cubic meter range. The techniques for these procedures are introduced in the next chapter.

More recently, in 2001 and 2002, the gases and dust released during and following the collapse of World Trade Center towers as well as that found in the aftermath of Hurricane Katrina in 2005 had to be analyzed.

Each of these examples suggest that air toxics sampling is complex and expensive and requires careful attention to quality assurance.

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QUESTIONS

1. Describe the four components of a sampling system.
2. List three examples of the four components, e.g., a metal bellows pump.
3. A solid sorbent Tenax cartridge has a capacity of 100 μg of toluene. If samples were collected at a rate of 5L min^{-1} , calculate the maximum ambient concentration which can be determined by an hourly sample and a 15-min sample.
4. Describe the sampling approaches used for air pollutants by your state or local government.
5. List the possible sources of loss or error in sampling for particulate matter.
6. Why is sampling velocity not an important parameter when sampling for gases?
7. List the advantages of passive sampling systems.
8. Describe the precautions which should be considered when determining the location of the sampling manifold inlet for an ambient monitoring system.
9. What is the concentration of particle-phase mercury in the air if sample shows that the average (mean) particle concentration ($\text{PM}_{2.5}$) is $1.5\ \mu\text{g m}^{-3}$ and the mean concentration of mercury on the particles in the sample is $10\ \text{ng g}^{-1}$?
10. How important is the rest of the PM fraction ($\text{PM} > 2.5\ \mu\text{m}$) in the above scenario? Explain.

11. How might a sample be analyzed in the above question's scenario (both the particle and the metals sorbed to the particle)? What are the advantages and disadvantages of each of the major types?
12. In the above examples, what might be some of the important differences in the physical and chemical characteristics between mercury and cadmium in sampling.
13. What if you wanted to know a particular species of mercury (e.g. mercury chloride or non-methyl mercury)? Can you use a technique like X-ray fluorescence? Why or why not? What might have to be done to be able to answer this question; i.e., what are the key features needed in your sampling and analysis plan?
14. What is the concentration of benzo(a)pyrene (B(a)p) in the scenario in Question 9 if its concentration on the particles (mean) is 10 ppb? How would you collect samples for gas phase B(a)p? How might this differ from the method used for mercury?