Section I
Sample Preparation and Sample Pretreatment

Introduction

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In order to obtain high-quality analytical data, the primary objective of the analytical scientist must be, ideally, to obtain an artifact-free sample for the analysis. This is seldom a simple matter and presents many challenges to the investigator. It is often the case that many sampling programs frequently select the sampling methods based on what equipment is available rather than on what question is to be answered or what problem is to be addressed. It is important that sampling objectives be defined first and then a suitable method be selected. The question, "Can the sampling method I select provide me with the answers I am looking for?" must always be answered in the affirmative.

Sampling methodology differs greatly depending upon whether the sample is in the gaseous, liquid or solid phase. If the sample is in the liquid or solid phase, is the sample an aerosol or particle that exists in a particular gaseous phase? In or on what medium shall the sample be collected and retained? How shall the sample be stored and/or transported prior to analysis? Must the sample be processed before the analysis to concentrate or isolate the analyte(s) of interest from the sample matrix before analysis? If the sample is to be used for legal purposes, a chain of custody (not discussed here) needs to be developed. A Quality Assurance/Quality Control (QA/QC) program will likely have to be developed for the analytical method.

In situations where the analyte is present in trace quantities (as usually occurs in environmental samples), it is vitally important to maximize the recovery of the analyte from the sample matrix and to lose as little of the analyte as possible during any subsequent processing or "work-up" stages in the analytical process. Extensive recovery testing is usually required to determine the efficiency of the collection and processing procedures.

The following two chapters address the question of sampling methods for the three phases in which a sample may occur – gaseous, liquid and solid. Different sampling approaches (active vs. passive) are considered as are the specific approaches for a wide variety of sample types and matrices.

1

Collection and Preparation of Gaseous Samples

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1.1
Introduction

The collection of artifact-free gas phase samples is not a simple process. Unless the gas is a highly filtered and purified gas, it will most likely be a complex mixture of gases and vapors, liquids (aerosols) and solids (particles). For example, one of the most sampled, yet most complex sources is the earth's atmosphere. The atmosphere is a mixture of gases (both organic and inorganic), liquids (such as rain droplets and aerosols) and solids (particles such as windblown dusts, pollens and fly ash from a myriad of combustion processes). The atmosphere is also irradiated with sunlight, which can initiate many photochemical reactions. It can truly be said that the atmosphere is like a giant chemical reactor in which all but the most inert compounds are chemically modified, dispersed and eventually deposited to the earth [1]. It is not a simple matter to collect atmospheric samples, or other gaseous samples for that matter, without modifying the sample during the collection process. After all, one really wants to know the gaseous composition at the time of collection, not as modified by a particular sampling process.

Prior to using the sophisticated techniques described in the rest of this book to analyze a sample, one must first collect the sample and then prepare it for the final analysis. Analytical techniques have become incredibly sophisticated and more selective and sensitive over the past 20 to 30 years. Sampling methods, unfortunately, have not kept pace with the advances in the analytical technology despite the fact that a poorly collected sample, no matter how sophisticated the analytical method, will still yield a poor result. To borrow an expression from the computer industry: "Garbage in equals garbage out". The ultimate challenge is to collect a sample that reflects the composition of the sample at the time of collection. To achieve this objective, the sample collection method selected must be as free as possible from all artifacts of the sampling procedure and be appropriate for the objective of the program for which the measurements are made. It is just as important to maintain the integrity of the sample after the sampling has been completed and during any work-up procedure to prepare the sample for analysis.

An artifact is something not naturally present in the sample but is introduced during the sampling or work-up procedure. Artifacts include the oxidation of the collected sample during the sampling process, adsorption of gas phase compounds by a particle collection filter, volatilization of particle associated compounds that subsequently are trapped by an adsorbent and assessed as gas phase material, irreversible adsorption or reaction of the gases or vapors with the sampling substrate, condensation of water on the sample, loss of adsorbed sample during sampling, transport or sample work-up and chemical alteration of the sample during sample extraction and/or preparation. There are many other potential artifacts, all of which should be minimized. Part of this process is the selection of the proper sampling method for the problem at hand.

Since the focus of this book is the analysis of collected samples, only integrated samples will be considered here. Furthermore, this chapter will look only at the collection and preparation of gaseous samples. The collection of particle and liquid samples will be considered in the following chapter. Because of their complexity, most of the discussions in this chapter will center on the collection and analysis of atmospheric samples, however, the principles involved relate to any gaseous sample.

The most important aspect of sampling is to know what problem is to be solved or addressed and then to select the appropriate method. Proper selection of sampling method is critical to the solution of a problem.

1.2
Sampling considerations

In the atmosphere, gases and vapors co-exist as gas phase material. Each chemical has its own vapor pressure and saturated vapor concentration. Chemical compounds that have a subcooled liquid phase vapor pressure greater than approximately 10^{-2} Pa will exist entirely in the gas phase. These compounds include gases such as ozone, oxides of nitrogen, carbon monoxide, carbon dioxide and sulfur dioxide and vapors from volatile organic compounds (VOCs), such as methylene chloride, acetone, and isoprene, low molecular weight aliphatic compounds and aromatic compounds such as benzene, toluene and xylene. Contaminants with subcooled liquid phase vapor pressures less than 10^{-5} Pa will exist almost entirely in the particle phase, while contaminants with vapor pressures between 10^{-2} and 10^{-5} Pa will partition themselves between the gaseous and particulate phases. These are the so-called semivolatile organic compounds (SVOCs), and include many of the polychlorinated biphenyls (PCBs), some of the polycyclic aromatic compounds, many of the dioxins and many pesticides. Semivolatile compounds exist in the atmosphere at or near equilibrium between the gaseous and particulate phases. In Fig. 1.1, the gas phase fraction of SVOC components is plotted versus the log of the subcooled liquid phase vapor pressure (log P_L) of the SVOCs. This shows graphically that compounds with a log P_L between approximately 10^{-2} and 10^{-5} Pa will partition between the gaseous and particulate phases in the atmo-
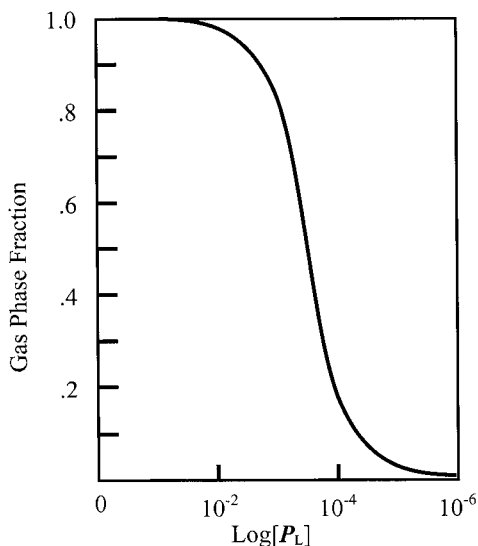
Fig. 1.1 Gas Phase fraction as a function of the log of the subcooled liquid vapor pressure (Pa) of SVOCs.

sphere. First described by Junge [2], the theory has been greatly developed by Pankow [3, 4] and Pankow and Bidleman [5].

The sampling method selected must be sensitive to the vapor pressure of the compound, the temperature at which sampling is to take place, the stability of the compound during sampling and the anticipated concentration of the compound in the air. The act of drawing an air sample through a sampler requires a pressure drop across the sampler and this will disturb the equilibrium between the gas and particle phases. Sampling methods must endeavor to minimize this disruption of the equilibrium if gas particle partition measurements are being made.

Since gaseous samples are about 800 times less dense than liquid or solid samples and, since the vast majority of these gases and vapors exist in the atmosphere in extremely low concentrations (often at nanogram to sub-nanogram per cubic meter concentrations), it is necessary to collect large volumes of air in order to collect sufficient material to permit both qualitative and quantitative analyses. For example, in gas chromatographic/mass spectrometric analyses, 1 µL of a 1 mL sample will typically be injected onto the column of the gas chromatograph. If the instrument has sufficient sensitivity to permit quantitation on 50 pg of analyte, then there must be 50,000 pg or 50 ng of the analyte in the 1 mL sample. This, in turn, requires that 50 ng of sample be collected from the air (assuming no losses during the work-up procedure). If the sample exists in the air at a concentration of 1 ng m^{-3}, then it follows that one would need to collect a minimum of 50 m^3 of air for the analysis. Likewise, if the compound exists in the air at a concentration of 100 ng m^{-3}, then one need only collect a 0.5 m^3 sample. It is, thus, important to have some knowledge of the anticipated concentration of the analyte in the gas mixture prior to selecting the sampling method and sampling time.

To collect such large volumes of air, ambient air sampling is frequently conducted over many hours, usually 12 h or 24 h. These are termed integrated air samples. Air samplers frequently draw air through a filter to remove the particles, then through a sorbent material to trap the gaseous components. In this filter/sorbent geometry air sampler, it is now well known that artifacts are produced, the most serious of which is the volatilization of the particle adsorbed semivolatile compounds due to the pressure drop across the filter. These volatilized compounds pass through the filter and are trapped on the adsorbent where they are analysed as though they were gaseous compounds. Temperature variations during sampling will also influence the gas/particle partitioning of the SVOCs. The filter sorbent geometry should be restricted to determining the total combined gas and particle burden of a particular air sample but should not be used to determine gas/particle partition ratios of semivolatile compounds. If the gas/particle partition ratios are to be determined, it is preferable to remove the gas phase first, and then to remove the particles, as is done in the annular diffusion denuder samplers.

The sample must subsequently be extracted from the trapping medium and processed before it is analysed by the desired analytical method. Very often the processing requires a series of steps to isolate a particular compound or compound class for the analysis to be effective. If the work-up steps are ignored, the collected sample is usually too complex for even the most selective and sensitive analytical methods available today.

If the concentration of the analyte fluctuates with time, then the result of the sampling is a concentration averaged over the sampling time period. The shorter the sampling period, the greater will be the temporal resolution of the concentration variations of the analyte.

Many chemical species found in the atmosphere are chemically and/or photochemically reactive. If such compounds are present, inert sample inlets and surfaces must be employed since there is a strong potential for the formation of artifacts. This is not a simple problem to overcome. It is also necessary to prevent further chemical degradation of the compounds during and after the sampling has been completed. The sample must not react with the sampling surfaces, filters or adsorbents. When adsorbents are used, the efficiency of extraction of the compounds from the adsorbents must be determined for each compound. If the gases and vapors pass through particle filters, the gases and vapors must not be adsorbed by, or react with the material from which the filters are made. Glass fiber and quartz fiber filters, for example, are well known to adsorb organic compounds whereas Teflon-coated glass fiber filters are much less likely to adsorb organic vapors. On the other hand, if the primary objective of the sampling is to determine the elemental carbon content of the collected particles, then a Teflon-coated glass fiber filter would obviously be a poor choice since the Teflon coating would become part of the analyte during the high temperature heating of the sample. As stated previously, it is imperative that the sampling system suits the problem that is to be solved. If adsorbents or diffusion denuders are used, it is possible that gas phase material adsorbed on the surfaces of the adsorbents might break through the collector. This must be investigated and, if significant, then either a different

adsorbing material must be used or a breakthrough factor must be statistically determined. All potential artifacts must be considered and minimized, if not eliminated, through proper sampler design and analytical process control. This often necessitates lengthy quality assurance (QA) and quality control (QC) programs.

1.3
Active vs. Passive Sampling

There are two basic means of collecting a gaseous sample: active sampling and passive sampling.

In active sampling procedures, air is drawn through an absorbing or adsorbing medium by a pump in order to trap the gas phase material. It is important that the sampler has an accurate, calibrated means to determine the total volume of the gaseous sample and the rate at which the gas is being sampled. This is most easily accomplished by the use of calibrated mass flow controllers.

In passive sampling devices, an adsorbing material is placed at a fixed distance away from the air being sampled. Gas phase molecules must pass through a membrane or filter and diffuse across this distance and be trapped on or react with the collecting medium. The principles of diffusion are utilized to calculate the concentration of the specified contaminant in the ambient air. The diffusion rate across the passive sampler (and/or through the membrane) is analogous to the flow rate in an active sampler.

1.3.1
Active Air Collection Methods

There are many active air sampling methods available. Each method utilizes different ways to collect gaseous samples and each sampling method has its own particular inherent artifacts, and, thus, each method has its own strengths and weaknesses. It cannot be stated too often that the appropriate sampling method must be selected to address a particular question or problem.

There are several basic mechanisms whereby gases and vapors may be collected for subsequent analysis. Gaseous samples may be adsorbed on the surface of various substances, which have large surface areas and are specifically designed to collect the gaseous chemical species desired. They may react chemically with some chemical adsorbed on the surface of the collection device or on particles in the collector. Gases may be collected in bags or canisters or trapped in bubblers, in mist chambers or cryogenically. Each of these methods will be described briefly below.

1.3.1.1 **Sorbents**

Sorbents come in many varieties and may be used as beds (packed in glass or metal tubes), surfaces (deposited on tubular or annular surfaces) or in chemically treated filters designed to trap compounds selectively. They may be organic polymers, inorganic materials or made from activated carbon. Each sorbent material has specific advantages and disadvantages in specific sampling situations. Some sorbents are chemically treated to react with a single component and are used in specific gas samplers. They indicate the presence of a gas by a color change and the concentration of the gas by the length of the color developed in the adsorbent column. Since these sorbents give a direct indication of the gas concentration, no further analysis is performed. As a consequence, they are outside the scope of this book and will not be considered further.

Other sorbents are not compound specific and, as a result, trap a wide range of compounds. Unless specifically desired (see later in this section the discussion of DNPH-coated sorbents), it is vitally important that the compounds collected do not react with the sorbent. It is an unfortunate reality that the efficiency of recovery of most adsorbed compounds from the sorbents is less than 100 %. For this reason, the efficiency of the sorbent for the desired compounds and the extraction or desorption efficiency of the compounds from the sorbent must be determined.

Organic polymers have proven themselves to be effective adsorbents for many organic chemical species. They include materials such as Tenax™ (2,4-diphenyl-*p*-phenylene oxide), XAD (styrene-divinylbenzene copolymer) and polyurethane foam (PUF). Tenax and XAD are available as small beads (less than 1 mm in diameter) and have large surface areas for effective adsorption of organic chemicals. These materials are hydrophobic which makes them suitable for the collection of organic vapors in gases that contain a significant relative humidity. As water moisture causes significant problems for gas chromatographic analysis, the use of hydrophobic adsorbents can be a significant advantage. These resins are particularly effective for neutral and aromatic organics but are less effective in the trapping of highly polar organics. Under extremely moist conditions, however, these adsorbents may lose their efficiency, particularly if water condenses on the sorbent. PUF is suitable for the retention of polychlorinated organics such as the PCBs but is ineffective in trapping low molecular weight organics. PUF is not effective for trapping aromatics such as naphthalene, acenaphthene and acenaphthylene.

Although Tenax has good thermal stability it has a major disadvantage in that it is notoriously difficult to clean. The XAD resins also have good thermal stability but are still difficult to clean. If not manufactured from pure materials, solvent extraction or thermal desorption of the polymer will release the impurities present in the starting materials or produced during the manufacturing process. This problem is not easy to eliminate. For that reason, the sorbents must be exhaustively extracted or thermally desorbed prior to use. Tenax is cleaned by thermal treatment whereas the XAD resins are usually solvent extracted. Blanks are necessary to establish the level of interferences to the analytical procedure. In addition, the sorbents, although extremely efficient for the trapping of the higher molecular weight organics, are less effective in trapping and retaining the lower molecular weight VOCs.

Carbon-based traps have a lower affinity for water than does Tenax, but they must be purged with ultra-pure helium while being heated to drive off adsorbed impurities. Surrogates should be added before this clean-up procedure to determine the efficiency of the purge. After activation, sorbents must be handled with care as they may adsorb organic vapors from the air, thus resulting in adsorption artifacts.

Because of their physical structure and specific surface area, polymeric sorbents have a finite capacity for the collection of organic compounds. It is, therefore, necessary to determine the capacity of a particular sorbent under the particular sampling conditions desired. The minimum sampling duration will be defined by the concentration of the organics in the sampled gas and the sampling rate. If the capacity of a sorbent is exceeded, breakthrough of the sample will occur. In practice, it is wise, if not necessary, to use two sorbents in tandem. Any compounds which break through the first sorbent will be trapped by the second sorbent. This will indicate the extent to which breakthrough is a problem.

Adsorbents such as XAD can be ground to sub-micron sized particles thus greatly increasing their surface area and capacity. When these particles are properly applied to concentric glass tubes called annular diffusion denuders, they provide a large surface area for the collection of gases and vapors. Passing air through these devices will result in the gases and vapors being adsorbed to the walls of the denuder. The particles, because of their greater mass and momentum, pass through the denuder and are trapped by a filter. This sorbent/filter geometry greatly reduces the artifacts inherent in the filter/sorbent geometry.

PUF has commonly been used downstream of a particle filter to collect the gas phase material that passes through the filter. PUF is reasonably effective in trapping the higher molecular weight organics, but, like the resins, it is much less effective in trapping the low molecular weight organics. PUF is also notoriously difficult to clean and is well known to undergo chemical degradation when exposed to atmospheric oxidants. This can be seen over the course of a single 12 h sample by a yellowing of the foam that remains after solvent extraction.

Inorganic sorbents include silica gel, alumina and molecular sieves. Because they are polar substances, they are particularly effective in trapping polar vapors. For these sorbents, it is the degree of polarity which determines how well a particular gas or vapor is retained. A source of potential error is that very polar gases may displace less polar compounds from the adsorbent. For atmospheric sampling this presents a significant problem in that these sorbents are also very efficient in collecting water, which can cause serious deactivation of the sorbents. As a result, these compounds are not often used for the collection of organic vapors.

An adsorbent such as silica may be treated chemically with, for example, 2,4-dinitrophenylhydrazine (DNPH). When an air sample is passed through this material, organic carbonyls react with the DNPH to form the dinitrophenylhydrazone which can then be extracted and easily detected. In such a system, the sorbent simply acts as a large area substrate for the chemical reactant.

Activated carbon in beds and impregnated in glass fiber mats has been used to collect organic vapors. These sorbents are relatively non-polar and trap a wide

range of organics. It is extremely difficult to remove adsorbed organic compounds from activated carbon sorbents. This limits their applicability in air sampling unless the sole purpose of the adsorbent is to remove organics from an air stream.

1.3.1.2 Bags

Bags made of aluminum/plastic or of plastic laminates can be used to collect gaseous samples. They are filled either with inert surface pumps or indirectly by placing the bag in a non-flexible, closed container and evacuating the space between the bag and the container. When the space between the bag and the rigid container is evacuated, the bag will inflate, drawing in the air sample. Bags must be carefully cleaned and examined and tested for leaks prior to sampling. Loss of organics to the walls can be a significant problem. Diffusion of gases and vapors through the walls has been greatly reduced by the use of the laminated plastics. The use of bags allows a grab sample of air, usually less than a cubic meter in volume, to be collected. Because a relatively small volume of air is collected, the compound of interest must be in sufficiently high concentration that it can be detected and quantified. Bag collectors can be bulky and difficult to transport.

If the collected sample is to be analysed by a technique such as gas chromatography-mass spectrometry, the sample must be passed through an adsorbent to concentrate the hydrocarbon gases and vapors. The sample must then be released from the adsorbent, either by solvent extraction or thermal desorption, prior to injection into the gas chromatograph.

1.3.1.3 Canisters

Air may be collected in glass or steel containers. Glass containers may be evacuated prior to sample collection or the air sample may be drawn through the container. Glass containers, because of their small size, allow only the collection of a grab sample. Steel canisters with electropolished or chemically deactivated interiors may also be used to collect air samples. Inner surface treatment is necessary, as stainless steel is an adsorptive medium. Most canisters are designed to be evacuated in the laboratory then transported to the sampling site. However, prior to use, the canisters must be cleaned. This is a laborious procedure that requires that the canisters be evacuated to below 0.05 Torr and heated for several hours. The procedure may have to be repeated several times if the canister was previously exposed to a "dirty" sample. Even this may not satisfactorily clean a "dirty" canister. The canister may have to be wet cleaned to remove some polar compounds.

A valve in the canister is opened to allow the air sample to leak into the canister at a defined rate. The leak rate is fixed, often by a use of a suitable critical orifice. Depending on the leak rate, the size of the canister and the initial vacuum, the canisters may collect short-term grab samples or may extend the collection process up to as long as 48 hours, although sampling times of 6 to 8 hours are more common. Canisters have been used primarily to collect VOCs. Water management is a major problem with canisters and, to reduce its effects, Nafion drying tubes may have to

be used in the sampling inlet. The gases collected in these canisters remain stable and do not alter their concentrations over several weeks of storage. Canisters can be much larger than glass containers and come in sizes from 1 to about 35 L.

Some canisters have been designed to be pressurized to approximately 30 psi. However, this necessitates that the air sample passes through the sampling pump. As a result, the sampling pump has a great potential to contaminate the sample.

Prior to analysis, the collected sample must be treated in a manner similar to that for bags. The collected sample must be concentrated on a suitable sorbent trap, then eluted or desorbed from the trap before it is injected into the separation and analysis instrumentation.

1.3.1.4 **Bubblers**

Gases that are not easily adsorbed on an adsorbent may be more easily collected in a liquid bubbler or impinger. Air is drawn into the bubbler or impinger and is scrubbed by the trapping liquid. The air frequently passes through a glass frit to form tiny bubbles. This increases the surface area of the bubbles and promotes effective exposure of the gas to the trapping liquid. The gases or vapors may simply be dissolved in the liquid, or they may react chemically to form more stable complexes. If the rate of uptake of the analyte is faster than the time needed for the bubbles to pass through the bubbler, then the gas will be retained. Impingers may contain as little as about 5 mL of liquid up to several hundred mL of liquid. For long sampling periods, there is the danger that the sorbing liquid may evaporate. This may, in turn, limit the effective sampling time. To counter this problem, devices have been developed to maintain a constant volume of liquid in the bubbler. Alternatively, organic solvents may be placed in sub-ambient temperature baths to minimize evaporation losses. It is necessary to have an *a priori* knowledge of the concentration of the contaminant in the air so that an appropriate impinger size can be selected. It is, of course, vitally important that the solution used in the bubbler does not freeze under the sampling conditions.

As in the case of sorbent tubes, breakthrough may pose a problem, particularly if the gas flow rate is too high and an efficient scrubbing of the gas does not occur. To avoid such a problem, two or more bubblers may be placed in series.

With increasing attention being paid to the chemical nature of particles and the effect that they may have on gas analysis, it may be necessary to remove particles from the air sample upstream of the bubbler. In fact, it may also be necessary to remove undesired gases before the bubbler if they are known to interfere with the determination of a particular analyte.

The sample from bubblers is already in the liquid phase but the sample may have to be reduced in volume to concentrate further the compounds of interest prior to injection into the separation and analysis instrumentation. If the sample is collected in an aqueous solvent and water poses a problem for the analytical instrumentation, the chemicals of interest will have to be extracted into an alternative solvent that is compatible with the analytical instrumentation.

1.3.1.5 Mist Chambers

Mist chambers function in a manner very similar to that of bubblers. In the mist chamber, a fine mist of water or other chemical is generated. The air sample is drawn into the mist chamber and the analyte is scavenged by the mist droplets. In these chambers it is not clear to what extent particles are scavenged. If particles are not to be sampled, then particle filters may be placed before the mist chamber. This, however, may result in the volatilization of particle-associated organics, as described previously. If water is used as the scavenging mist, the analytical method must be able to accommodate water.

1.3.1.6 Cryogenic Trapping

Cryogenically trapping contaminants from air is attractive since a wide range of gases, both organic and inorganic, are collected. In addition, contamination problems, inherent in many types of samplers, are eliminated and compound recoveries are consistent. Problems may occur if using liquid nitrogen as the cryogenic medium. Under liquid nitrogen temperatures, oxygen, water and carbon dioxide from the air will liquefy and be trapped as well. Organic and inorganic compounds may undergo oxidation under these conditions. Water and carbon dioxide may cause significant problems in chromatographic systems.

   Prior to analysis, the cryogenically trapped compounds must be warmed and released while trapping the compounds of interest. The analytes may be taken up in a liquid or passed through an adsorbent for concentration before injection into the analysis instrumentation.

1.3.2
Passive Sampling

Passive samplers place an adsorptive surface (frequently charcoal-based) a fixed distance from a windshield or semipermeable membrane in an enclosure in which the windshield or membrane is exposed to the air being sampled. These devices generally require that a minimum air movement across the windshield or membrane occurs in order to ensure that the device is sampling properly. The concentration of the contaminants of interest will determine the minimum exposure time of the passive sampler. The major advantages of this type of sampler are that the collection devices are small, require no electrical power and are very easy to use. After exposure, which can, for some devices, extend to periods as long as 6 months or more, the adsorbent is removed and extracted. The extract may have to be reduced in volume prior to analysis. As with other non-specific adsorbents, the passive sampler adsorptive surface will trap a wide variety of compounds. Oxidation of the adsorbed compounds may be a problem if the passive sampler is left for a long period in a gas that contains oxidants.

1.4
Extraction and Preparation of Samples

Regardless of the method of collection of an air sample, the ultimate objective is to remove the collected sample and prepare it for analysis. Adsorbents such as carbon, XAD, alumina, and silica gel are usually solvent extracted with solvents appropriate for the desired analytes, whereas Tenax is usually thermally desorbed. Carbon and carbon-based adsorbents may also be thermally desorbed. Regardless of the removal mechanism, the efficiency of the retrieval of each compound must be determined.

Solvent extraction of adsorbents is usually relatively efficient and reproducible. Large volumes of solvent may be necessary to extract the sample from some adsorbents. The greater the volume of solvent, the more dilute will be the analytes. Consequently, the extract must be reduced in volume (see below). The advantage of solvent extraction is that only a single aliquot of the final reduced extract is consumed in the analytical procedure. The disadvantage is that only 0.1 % to about 0.5 % of the sample can be analysed at a time. This, in turn, means that large sample volumes must be collected in order to get sufficient material to detect and quantify.

It is important to know the efficiency of the solvent extraction process. Aliquots of solutions of perdeuterated chemical standards can be spiked onto the sorbents prior to extraction. The perdeuterated analogs of the analytes of interest have different retention times in chromatographic systems so that they are easy to detect. By evaluating the amount of standard extracted, one can determine the extraction efficiency of the compounds of interest.

Thermal desorption of analytes from sorbents such as Tenax and carbon has the advantage that the entire sample can be used in the analysis. The disadvantage is that one gets only a single chance to analyze the sample, replicate samples are not possible. Smaller sample volumes can, however, be collected. The desorption temperature must be selected carefully to avoid decomposition or pyrolysis of the analytes. If the desired analytes are labile, then thermal desorption is not a viable removal method.

Liquid extracts will have to be reduced in volume prior to analysis to concentrate the extracted analytes to a level that can be detected in the analytical devices. Solvent reduction is usually done in an evaporation device in which the liquid is heated under vacuum. Because reduction under vacuum and heat can result in the loss of the more volatile analytes and possibly chemical reactions, internal standards with similar properties to the analytes should be added before the reduction is commenced.

Class separation or clean-up as it is also termed, may or may not be included in the analytical procedure. If the sample extract is exceedingly complex, containing hundreds of compounds, then a class separation may be desirable. This may be accomplished using column chromatographic methods, high-pressure liquid chromatographic techniques or solid-phase, micro-extraction methods. The objective is to separate the sample into a range of compound classes such as non-polar compounds and polar compounds. Subsequent analysis of the fractions collected will simplify the chromatographic steps needed to analyze the sample.

1.5
Summary

In this chapter, the basic methods for the collection of gases and vapors have been discussed. Although the primary examples are drawn from atmospheric sampling, the general principles should apply to the sampling of any gas or vapor for subsequent analysis.

One of the unavoidable consequences of collecting a gaseous sample for detailed chemical analysis it that there is, in all likelihood, no 100 % artifact-free sampling method, particularly if one is dealing with SVOCs. It is very difficult to ensure that a collected sample is truly representative of how things existed in the original gaseous sample. The basic objective of sampling must be to understand the complexity of the gas being sampled, define the problem that is to be solved, select a sampling method best suited to the sampling objectives and finally to understand and to minimize the occurrence of artifacts.

There are many excellent books and articles describing collection and analytical methods for specific gases and vapors. Below, are listed only a few of the many possible sources that treat the subject of collection and treatment of gases and vapors [6–10].

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