

Chapter  
**6**

*This chapter will take approximately 1 hour and 45 minutes to complete.*

# Gaseous Sampling

## OBJECTIVES

### Terminal Learning Objective

At the end of this chapter, the student will be able to describe the absorption and adsorption process and the devices used that affect collection efficiency.

### Enabling Learning Objectives

- 6.1 Summarize the operating principles of absorption when sampling gaseous pollutants.
- 6.2 Identify the types of absorption and the factors affecting collection efficiency.
- 6.3 Determine the methods of collection efficiency.
- 6.4 Summarize the operating principles of absorption when sampling gaseous pollutants.
- 6.5 Identify the types of absorption and the factors affecting collection efficiency.
- 6.6 Determine the methods of collection efficiency.
- 6.7 Summarize the operating principles of adsorption when sampling gaseous pollutants.

## 6.1 Principles of Absorption

### Introduction

Absorption of pollutants in various media plays an important role in air pollution monitoring. It is particularly important in the wet-chemical methods of analysis. Before the advent of continuous monitoring instrumentation, techniques employing absorption were the most inexpensive and up-to-date methods available.

Absorption is the process “of transferring one or more gaseous components into a liquid or solid medium in which they dissolve.” Absorption of gaseous pollutants in solution is frequently utilized in atmospheric sampling because of the numerous methods available to analyze the resulting solution. These methods include photometric, conductimetric, and titrimetric techniques. Details of sampling and analysis of specific gaseous pollutants by absorption are given elsewhere. This discussion concentrates on a description of the gas-liquid absorption process and factors affecting collection efficiency. Devices frequently utilized in gas-liquid absorption and several current applications are also discussed.

### Types of Absorption

In gas-liquid absorption the collecting liquid (i.e., the absorbent) may change either chemically or physically, or both, during the absorption process. In gas-liquid absorption sampling, two types of absorption have been recognized: (a) physical absorption and (b) chemical absorption.

A typical chemical absorption process would involve drawing a volume of air through a solution that reacts with the gaseous contaminant to form a nongaseous compound; for example, an acid mist is drawn through a volume of sodium hydroxide. The acid reacts with the base to form a stable salt. Titration of the unreacted base with standard acid indicates the quantity of pollutant reacted.

**Physical Absorption**

Physical absorption involves the physical dissolving of the pollutant in a liquid. The process is usually reversible in that the pollutant exhibits a relatively appreciable vapor pressure. The solubility of the pollutant in a given absorbent is dependent on the partial pressure of the pollutant in the atmosphere and the temperature and purity of the absorbent. An ideal solvent would be relatively nonvolatile, inexpensive, noncorrosive, stable, nonviscous, nonflammable, and nontoxic. In many cases distilled water fulfills many of these characteristics and is used as the solvent for collecting some gases. The suitability of distilled water for several selected gases is presented in Table 6-1.

**Table 6.1. Solubility of selected gases in distilled water at 20°C.**

Gas	Volume absorbed per volume of water*
Nitrogen	0.015
Oxygen	0.031
Nitric oxide	0.047
Carbon dioxide	0.878
Hydrogen sulfide	2.582
Sulfur dioxide	39.374

\*Gas volumes reduced to 0°C and 760 mm Hg.

The physical absorption process involves collecting the pollutant by solution in the absorbent. The solution is then analyzed for pollutant concentration by a convenient analytical method. In general, low efficiency will be obtained for physical absorption unless the pollutant is very soluble and the ratio of dissolved gas to liquid volume is small. For this reason, physical absorption is rarely the only absorption process involved in collecting gaseous pollutants.

**Chemical Absorption**

In contrast to physical absorption, chemical absorption is a process that involves a liquid absorbent that reacts with the pollutant to yield a nonvolatile product. The solvent selected is one that reacts with the pollutant in an irreversible fashion – for example, the reactions of ammonia and carbon dioxide gases with acidic and basic solvents, respectively. These reactions produce carbonic acid (H<sub>2</sub>CO<sub>3</sub>) and ammonium hydroxide (NH<sub>4</sub>OH). The solubilities of these acids and bases are much greater than gaseous CO<sub>2</sub> or NH<sub>3</sub>. Primary factors affecting the choice of an absorbent in chemical absorption are the solubility of the pollutant, reactive properties of pollutant and absorbent, and the subsequent analytical method to be used. Care should be taken to avoid an absorbent that will interfere with subsequent chemical analysis.

A typical process involving chemical absorption is the reaction of SO<sub>2</sub> and aqueous H<sub>2</sub>O<sub>2</sub> to produce sulfuric acid. The concentration of SO<sub>2</sub> is determined by titrating the H<sub>2</sub>SO<sub>4</sub> formed with Ba (ClO<sub>4</sub>)<sub>2</sub>. This procedure is currently the

reference method for determining SO<sub>2</sub> emissions from stationary sources. However, today, an automated continuous equivalent method (e.g. UV Fluorescence) which provides real-time data would be used.

## 6.2 Collection Efficiency

Each absorption sampling device must be assembled from units found to be most suitable for the specific pollutant involved. It is not necessary to have 100% collection efficiency; however, the efficiency under sampling conditions should be known and reproducible. In some circumstances a sampling system having relatively low collection efficiency (e.g., 60 to 70%) could be used, provided that the desired sensitivity, reproducibility and accuracy are obtainable. There is much information available in the literature concerning optimum flow rates for specific pollutants and collection efficiencies with respect to the pollutant and absorbent for many sampling devices. However, much more information is needed on the variation of collection efficiency with the rate of sampling concentrations of a variety of compounds, and the nature of the collecting medium. For available information on gas-liquid absorption theory and the mathematical treatment of the variables affecting collection efficiency, the reader is referred to the literature (see the reference section of this chapter). Some sampling methods prescribe specific procedures regarding collection efficiency. Method TO-10A, for the determination of Pesticides/PCBs in ambient air<sup>1</sup> discusses sampling (collection) efficiency and how it is to be determined. For our purposes, discussion will be limited to only a qualitative description of the factors affecting collection efficiency.

### Factors Affecting Collection Efficiency

The variables affecting the collection efficiency of methods that use absorbers for the collection of gaseous contaminants may be conveniently considered as: (a) those associated with the absorber, such as an acceptable flow rate, bubble size, and height of the liquid column; (b) the chemical characteristics of the sampling situation, such as the chemical nature and concentration of the pollutant in the air and the absorbing medium, the chemical nature and concentration of the absorbing solution, and the reaction rate; and (c) the physical characteristics of the sampling situation, such as temperature, pressure, and pollutant solubility.

### Absorber Characteristics

The gas flow rate through the absorber is one of the major factors determining the collection efficiency of an absorber. Absorption collection efficiency varies inversely with the flow rate. An increase in the flow rate through the solution will decrease the probability of adequate gas-liquid contact. In addition, high flow

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<sup>1</sup> Found in the U.S. EPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition.

rates increase the possibility of liquid entrainment in the effluent gas. If varying flow rates are used in sampling, a collection efficiency versus flow rate curve should be determined for each absorber and absorber type. All other variables (e.g., temperature, pollutant and absorbent types, etc.) should be held at the desired values.

The collection efficiency of the absorption process for a gas or vapor by chemical absorption or physical absorption depends on the probability of successful collisions of reagent or solvent molecules with gas molecules. For a given concentration of reagent, this probability of collision will depend on the surface area of the gas bubbles, on the length of the column of liquid through which the bubbles must pass, and on the rate at which they rise through the liquid: as the volume of individual bubbles decreases, the surface area presented to the liquid increases. Hence, smaller bubbles have a greater possibility of gas transfer into the absorbent phase. For this reason many absorption devices use fritted discs as opposed to injection-type dispersion tubes to achieve a smaller bubble size. However, due to possible surface reactions that can take place at the frit, fritted bubblers may not be appropriate for certain types of sampling (e.g., for ozone). The length of the column of liquid in the absorber is another prime factor affecting the collection efficiency. The longer the gas bubble is in contact with the liquid, the more pollutant is transferred. However, in many cases this variable cannot be used to its maximum advantage; for example, when the sampled pollutant has a low concentration in the atmosphere, it must be collected in a small absorbent volume so that it is in the sensitivity range of the subsequent analytical method to be used. Bubble rise time is a function of bubble size and absorbent height. A compromise is usually reached by having the smallest feasible bubble size combined with the highest absorbent column possible for the particular analysis.

### **Chemical Characteristics**

The best situation, with respect to collection efficiency, is to choose an absorbent with a very large capacity for absorbing the pollutant without building up appreciable vapor pressure. This can be accomplished by choosing a chemical reagent that reacts with the pollutant in an irreversible fashion – for example, the irreversible reaction that occurs when carbon dioxide is absorbed in a sodium hydroxide solution to form the carbonate ( $\text{CO}_3^-$ ) ion.

The concentration of the absorbing medium to be used is a function of the expected concentration of the contaminant encountered, and the rate of the particular chemical reaction being used. An excess of the reactant in the absorbing solution is preferable to ensure that all the pollutant is collected and that the reaction rate is at a maximum. Ideally the reaction should be instantaneous since the period of contact between the pollutant and the absorbent is a short one.

Since the rate of reaction is proportional to concentrations of the reacting substances, other variables being equal, the rate of the process falls off as the reaction proceeds. This phenomenon must be compensated for by increasing the concentration of the absorbing liquid, thereby forcing the reaction to approach completion rapidly.

### **Physical Characteristics**

The primary physical characteristics affecting collection efficiency are pressure, temperature, and pollutant solubility in the absorbing medium. In many sampling situations, these variables are fixed by ambient conditions.

The solubility of the pollutant in the absorbing medium is related to its partial pressure (by Henry's law), and the partial pressure of the pollutant in turn is related to its concentration. The net effect considering ideal gas behavior is that an increase in pollutant concentration in the air will result in an increase in pollutant solubility in the liquid. Increased pollutant solubility, other variables being equal, results in higher collection efficiency.

An increase in temperature enhances chemical reactions but decreases pollutant solubility in the absorbent. In most cases the net effect is a decrease in collection efficiency with increasing temperature.

## **6.3 Determination of Collection Efficiency**

The method of determining collection efficiency will depend on how the results are to be used. If the most accurate values are needed, the best available method for determining collection efficiency should be used. On the other hand, if only approximate values are needed, a less stringent method for determining collection efficiency may be satisfactory. In all cases collection efficiency should be defined with respect to the method of determination.

The most accurate method of determining the collection efficiency of a particular absorber is by a trial on a synthetic atmosphere, duplicating in every respect the actual sampling conditions. Calibration techniques consist of both dynamic dilution and static dilution systems. In dynamic dilution, a continuous supply of a known pollutant concentration is available that can be sampled, while the static system consists of a container holding a known volume of pollutant of a known concentration. In both of these calibration procedures the investigator must be assured that the atmosphere being sampled actually contains the pollutant concentration it is believed to contain.

Another method that may be used for collection efficiency calibration is the comparison of the technique of interest to a previously calibrated method. In this technique the conditions of the calibrated method are imposed on the method of interest. All variables in both methods should be identical, especially with respect to interferences.

### **Absorption Devices**

A variety of devices have been used for sampling pollutants from the atmosphere. One of the simplest and most common devices used is an ordinary gas-washing bottle containing the absorbent plus a gas-dispersion tube for introduction of the pollutant into the solution. A typical device of this type is illustrated in Figure 6-1.

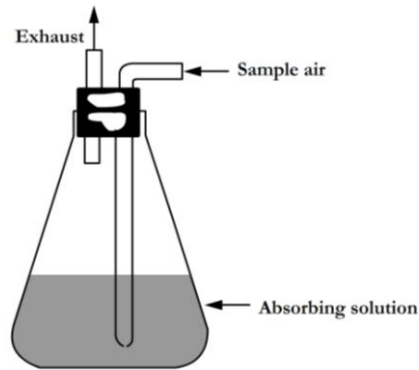


Figure 6-1. Absorption device adapted from an Erlenmeyer flask.

Gas flows from the unrestricted opening into the absorbent solution. A variety of absorbers of this type are available. They are usually glass and may be conical or cylindrical in shape. Typical flow rates through the various devices range from 1 to 5 liters per minute.

The majority of other absorption devices used in atmospheric sampling fall into two categories: (a) fritted-glass absorbers, “bubbler” and (b) impingers.

**Fritted-Glass Absorbers**

A great variety of shapes and sizes of these absorbers are being used. A few are illustrated in Figure 6-2.

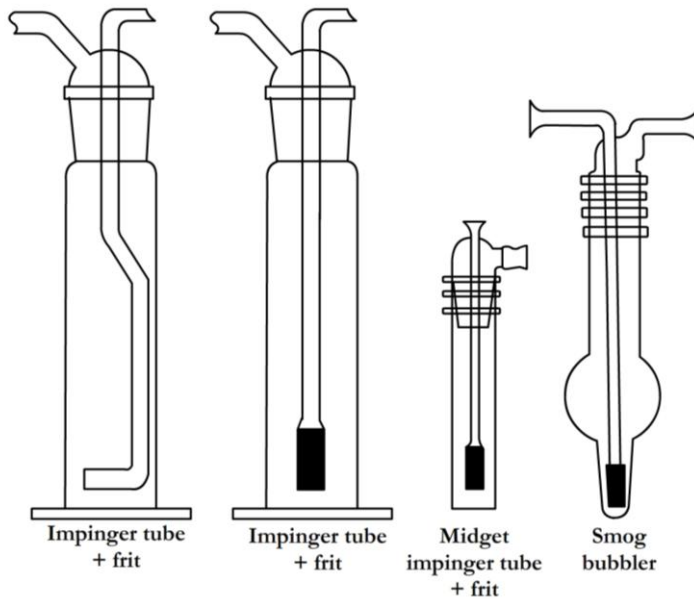


Figure 6-2. Typical fritted-glass absorbers.

These units usually provide the most efficient collection of gaseous pollutants. In addition to the commercially available units, homemade devices may be created using normal gas-dispersion tubes. The fritted part of the dispersion tube is readily available in the form of a disc or cylinder of various pore size. The coarse and extra-coarse frits provide good pollutant dispersion with a minimum head loss.

The collection efficiency of any one device will depend on the factors previously mentioned. However, under optimal conditions of flow rate, absorbing medium and pollutant type, many of the fritted-glass absorbers have a collection efficiency in excess of 90%. Several of their more important characteristics are presented in Table 6-2.

Table 6-2. Absorption sampling devices.

Principle of operation	Devices	Capacity (ml)	Sampling rate (L/min)	Efficiency* (%)	Comments
Simple gas-washing bottles. Gas flows from unrestricted opening into solution. Glass conical or cylindrical shape.	Standard	125–500	1–5	90–100	Bubblers are large. Reduction of sampling rate increases efficiency. Several units in series raises efficiency.
	Drechsel	125–500	1–5	90–100	Similar to above.
	Fleming	100	1–5	90–100	Difficult to clean.
Modified gas-washing bottles.	Fritted bubbler	100–500	1–5	95–100	Fritted tubes available for simple gas washing, items above. Smaller bubblers provide increased gas-liquid contact.
	Glass bead bubbler	100–500	1–5	90–100	Provides for longer gas-liquid contact, smaller bubbles.
Large bubbler traverses path extended by spiral glass insert.	Fisher Milligan bottle	275	1–5	90–100	
	Greiner-Friedrichs	100–200	1–5	90–100	Similar to Fisher Milligan.
Impingers – designed principally for collection of aerosols. Used for collection of aerosols.	Greenburg-Smith	500	1–5	90–100	Cylindrical shape.
Used for collection of gases. Restricted opening. Fritted tubes available which allow use of a bubbler.	Midget	100	0.1–0.5	90–100	
Smog bubbler.	Fritted bubbler	10–20	1–4	95–100	

\*Under optimum conditions of flow rate, absorbing medium, etc., for a particular pollutant.



Absorbers that use frits with a pore size of approximately 50 micrometers or less gradually become dogged with use. They may be cleaned by surging the appropriate cleaning solution back and forth through the frit and then rinsing with distilled water in the same fashion. Various substances may be removed from the frits by cleaning with the appropriate solvent (e.g., hot hydrochloric acid for dirt, hot concentrated sulfuric acid containing sodium nitrite for organic matter, etc.).

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### Impingers

Impingers are often used in sampling for gaseous and vaporous pollutants from the atmosphere. Two types of impingers are shown in Figure 6-3.

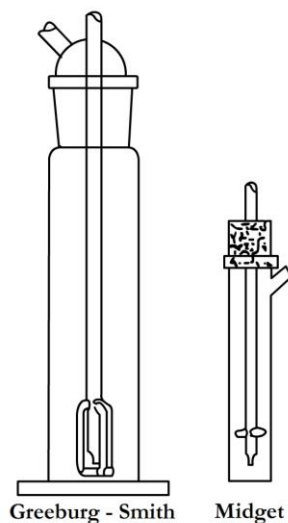


Figure 6-3. Two types of impingers.

A limited amount of investigation has indicated that the impinger is somewhat less efficient than the fritted absorber for collecting gaseous pollutants. When several types of absorbers were operated under optimal conditions, the midget impingers were found to be less efficient than the fritted-glass absorber. In addition, the threshold concentration for collection with the midget impinger was found to be somewhat higher than that for several types of fritted-glass absorbers. Unlike fritted-glass absorbers, impingers can also be used to sample for particulate matter.

**Summary**

Gas-liquid absorption is the process by which a gaseous pollutant is dissolved in a liquid medium. If a chemical reaction occurs between the pollutant (absorbate) and absorbent, the process is termed chemical absorption, whereas physical solution of the pollutant in the absorbent is termed physical absorption.

The collection efficiency of any particular absorption process is a function of the characteristics of the absorption device, and the chemical and physical properties of the absorbate-absorbent pair. Collection efficiency should be determined for each sampling analysis situation by a method that gives the accuracy desired.

**Current Applications of Absorption in Atmospheric Sampling***Compendium Method TO-6: Determination of Phosgene in Ambient Air Using High Performance Liquid Chromatography (HPLC)*

An air sample is drawn through a midjet impinger containing 10 mL of 2% aniline/toluene by volume. Phosgene readily reacts with aniline to form carbanilide (1,3-diphenylurea), which is stable indefinitely. After sampling, the impinger contents are transferred to a screw-capped vial having a Teflon-lined cap and returned to the laboratory for analysis. The solution is taken to dryness by heating to 60°C on an aluminum heating block under a gentle stream of pure nitrogen gas. The residue is dissolved in 1 mL of acetonitrile.

Carbanilide is determined in the acetonitrile solution using reverse-phase HPLC with an ultraviolet (UV) absorbance detector operating at 254 nm. Precision for phosgene spiked into a clean air stream is  $\pm 15\text{-}20\%$  relative standard deviation. Recovery is quantitative within that precision, down to less than 3 ppbv.

## 6.4 Principles of Adsorption

**Basic Principles**

Adsorption is the phenomenon by which gases, liquids, and solutes within liquids are attracted, concentrated, and retained at a boundary surface. The boundary surface may be the interface between a gas and liquid, liquid and liquid, gas and solid, liquid and solid, or solid and solid. Of the various boundary surfaces, the adsorption mechanism between liquid and solid, and gas and solid have received the most attention—the former with respect to removal of substances from solution with a solid adsorbent (e.g., purification), and the latter with respect to removing gaseous pollutants on solid adsorbents of high surface area.

A solid adsorbent has a crystal lattice structure. The atoms at the surface of the lattice are arranged in a regular sequence, which depends on the particular solid's crystalline structure. The valence or other attractive forces at the surface of a solid are unsatisfied, or unsaturated, because they are not united with other atoms. As a result of this unbalanced condition, the solid surfaces will tend to satisfy their residual forces by attracting and retaining gases or other substances

with which they come in contact. This surface concentration of substance is the adsorption process. The attracted substance is known as the adsorbate, while the surface substance is called the adsorbent.

In air pollution work, adsorption techniques are commonly used for collecting a specific gas or combination of gases. A typical process consists of passing a gas stream through a container filled with an adsorbent such as activated charcoal, alumina, or silica gel. The gas is bound to the adsorbent by molecular forces and, if condensation does not occur, the gas remains physically and chemically unchanged. Following collection, the gas may be removed from the adsorbent for analysis or ultimate deposition by applying heat, passing inert carrier gases through the system, or treating chemically.

How is adsorption distinguished from absorption? In absorption the material is not only retained on the surface, but it passes through the surface and is distributed throughout the absorbing medium. The term absorption in many cases implies a chemical reaction between the absorbing medium (absorbent) and the collected substance (absorbate). For example, water is absorbed by a sponge and by anhydrous calcium chloride. However, various gases are adsorbed on the surface of activated carbon. Often when the true process is not known, the term sorption is used.

### **Types of Adsorption**

Investigation of the adsorption of gases on various solid surfaces has revealed that the operating forces are not the same in all cases. Two types of adsorption have been recognized: (a) physical, or Van der Waals', adsorption (physiosorption) and (b) chemical adsorption (chemisorption).

#### *Physical Adsorption*

In physical adsorption, the attractive forces consist of Van der Waals' interactions, dipole-dipole interactions, and/or electrostatic interactions. These forces are similar to those causing the condensation of a gas to a liquid. The process is further characterized by low heats of adsorption, on the order of 2 to 15 kilocalories per mole of adsorbate, and by the fact that adsorption equilibrium is reversible and rapidly established.

Physical adsorption is a commonly occurring process. For example, this is the type of adsorption that occurs when various gases are adsorbed on charcoal. If the temperature is low enough, any gas will be physically adsorbed to a limited extent. The quantity of various gases adsorbed under the same conditions is roughly a function of the ease of condensation of the gases. The higher the boiling point or critical temperature<sup>2</sup> of the gas, the greater is the amount adsorbed. This concept will be discussed in more detail subsequently.

#### *Chemical Adsorption*

In contrast to physical adsorption, chemical adsorption is characterized by high heats of adsorption, on the order of 20 to 100 kilocalories per mole of adsorbate, which leads to a much stronger binding of the gas molecules to the surface.

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<sup>2</sup> Critical temperature may be defined as that temperature above which it is impossible to liquify a gas no matter how high an external pressure is applied.

Heats of adsorption are on the same order of magnitude as chemical reactions, and it is evident that the process involves a combination of gas molecules with the adsorbent to form a surface compound. This type of adsorption resembles chemical bonding and is called chemical adsorption, activated adsorption, or chemisorption. For example, in the adsorption of oxygen on tungsten it has been observed that tungsten trioxide distills from the tungsten surface at about 1200 K. However, even at temperatures above 1200 K, oxygen remains on the surface, apparently as tungsten oxide. Additional examples of chemical adsorption are the adsorption of carbon dioxide on tungsten, oxygen on silver, gold on platinum, and carbon and hydrogen on nickel.

A comparison of physical and chemical adsorption can be made by considering the adsorption of oxygen on charcoal. If oxygen is allowed to reach equilibrium with the charcoal at 0°C, most of the oxygen may later be removed from the charcoal by evacuating the system at 0°C with a vacuum pump. However, a small portion of the oxygen cannot be removed from the charcoal no matter how much the pressure is decreased. If the temperature is now increased, oxygen plus carbon monoxide and carbon dioxide are released from the charcoal. Thus, most of the oxygen is physically adsorbed and can be easily removed, but a small quantity undergoes a chemical reaction with the adsorbent and is not readily removed. In some cases, chemical adsorption may be preceded by physical adsorption, the chemical adsorption occurring after the adsorbent has received the necessary activation energy.

In general, with respect to the adsorbent-adsorbate pairs, chemical adsorption is more specific in nature than physical adsorption. It is usually a much slower process, requiring the displacement or selection of the molecules where the reaction is to occur. The chemisorption process is enhanced at higher temperatures where existing energy barriers between the adsorbent and adsorbate are overcome. At low temperatures, chemical adsorption in some systems may be too slow to reach a measurable amount. In many cases the adsorption occurring is a combination of both types. At low temperatures physical adsorption may predominate, whereas at higher temperatures chemisorption may be more prominent. This situation is true for the adsorption of hydrogen on nickel. However, because of the non-specificity of Van der Waals' forces, physical adsorption may be occurring, but be hidden by chemisorption. Finally, chemical adsorption is usually limited to the formation of a single layer of molecules on the adsorbent's surface (monolayer adsorption), whereas in physical adsorption the adsorbed layer may be several molecules thick (multilayer adsorption).

In the use of adsorption equipment in air pollution control, physical adsorption plays the most prominent part.

### **Variables Affecting Gas Adsorption**

The quantity of a particular gas that can be adsorbed by a given amount of adsorbent will depend on the following factors: (a) concentration of the gas in the immediate vicinity of the adsorbent; (b) the total surface area of the adsorbent; (c) the temperature of the system; (d) the presence of other molecules competing for a site on the adsorbent; and (e) the characteristics of the adsorbate such as weight, electrical polarity, and chemical reactivity. Ideal physical

adsorption of a gas would be favored by a high concentration of material to be adsorbed, a large adsorbing surface, freedom from competing molecules, low temperature, and by aggregation of the adsorbate into a form that conforms to the pore size of the attracting adsorbent.

Several of the above listed variables will now be discussed in greater detail.

### **Adsorption Isotherms**

Adsorption processes where physical adsorption rather than chemisorption represents the final state can be explained in terms of equilibrium measurements. For a given amount of adsorbent with a given surface area, the amount of gas adsorbed is dependent on the pressure (or concentration) of the gas surrounding the adsorbent. The higher the pressure or concentration of the gas at a given temperature, the greater the amount of gas adsorbed. When an adsorbent and gas are mixed, the amount adsorbed will gradually increase while the concentration of the adsorbate in the system decreases until the rate of adsorption becomes equal to the rate of desorption. Thus, equilibrium between the two reactions is established. If additional gas is added to the system, the amount adsorbed will increase until equilibrium is again established. Likewise, if the gas concentration is decreased, the adsorbent will lose gas to its surroundings until equilibrium is again reached.

The description of the relationship between the quantity of gas adsorbed at various concentrations or pressures at constant temperature is called an adsorption isotherm. An adsorption isotherm consists of a plot of the data obtained from measuring the amount of gas adsorbed (e.g., grams adsorbed per gram of adsorbent) at various gas concentrations or pressures (e.g., moles per liter or atmospheres), as the case may require, at equilibrium under a condition of constant temperature. Adsorption isotherms are useful in that they provide a means of evaluating (a) the quantity of gas adsorbed at various gas concentrations; (b) adsorptive capacities at various gas concentrations; (c) the adsorptive capacity as a function of concentration and type of gas; and (d) the surface area of a given amount of adsorbent.

#### *Types of Adsorption Isotherms*

The graphic plots of adsorption isotherms yield a wide variety of shapes. Six general types of isotherms have been observed in the adsorption of gases on solids: these are illustrated in Figure 6-4. In physical adsorption all six isotherms are encountered, while in chemisorption only Type 1 occurs.

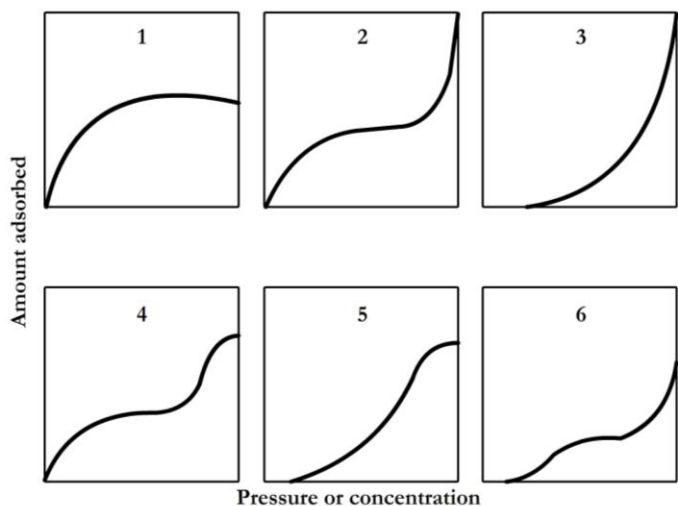


Figure 6-4. Gas adsorption isotherms.

Type 1 – This type represents the adsorption of a single layer of gas molecules on the adsorbent. There is no interaction between the adsorbed molecules.

Type 2 – This isotherm begins like Type 1 but is modified at high pressure by multilayer adsorption. There is definite interaction between the layers of adsorbed gas molecules.

Type 3 – This type of isotherm is rare. It occurs only when initial adsorption favors a very few strong sites. The interaction between adsorbed molecules is so strong that vacant sites next to occupied sites are stronger than any other vacant sites. In this type of adsorption the number of effective sites increases with coverage of the adsorbent.

Types 4 and 5 – These two are similar to Types 2 and 3 respectively, except that they continue to exhibit adsorption at high adsorbent coverage.

Type 6 – This type resembles Type 5 with monolayer adsorption first and then continued deposition of a multilayer film.

### Adsorbate Characteristics

The major adsorbate characteristics affecting the amount of gas adsorbed are the ease of liquefaction of the gas, adsorbate size, concentration of the gas, and presence of other gases.

#### *Gas Liquefaction*

The specificity by which certain gases are adsorbed on solid adsorbents is illustrated in Table 6-3, where the volumes of different gases adsorbed by one gram of charcoal at 15°C are tabulated.

Table 6-3. Adsorption of gases on one gram of charcoal at 15°C.\*

Gas	Volume adsorbed (cc)	Critical temperature (K)
H <sub>2</sub>	4.7	33
N <sub>2</sub>	8.0	126
CO	9.3	134
CH <sub>4</sub>	16.2	190
CO <sub>2</sub>	48.0	304
HCl	72.0	324
H <sub>2</sub> S	99.0	373
NH <sub>3</sub>	181.0	406
Cl <sub>2</sub>	235.0	417
SO <sub>2</sub>	380.0	430

\*Volumes of gases have been reduced to standard conditions (0°C and 1 atmosphere pressure).

Table 6-3 indicates that the extent of adsorption parallels the increase in critical temperature. This correlation suggests that gases which liquify easily (high critical temperatures) are more readily adsorbed. However, it does not imply that the adsorbates exist as liquids on the adsorbent's surface. A similar relationship is obtained with boiling points.

*Adsorbate Size*

The size of the gas molecule to be removed by adsorption is characterized by a lower and upper range. The lower size limit is imposed on physical adsorption by the requirement that the pollutant must be higher in molecular weight than the normal components of air. In general, gases with molecular weights greater than 45 are readily removed by physical adsorption. This size includes most odorous and toxic gases of air pollution interest. Gases of interest of lower molecular weight, such as formaldehyde and ammonia, may be removed by chemical adsorption methods using appropriately impregnated adsorbents. For the upper limit, the individual particles must be sufficiently small so that Brownian motion, or kinetic velocities, will ensure effective contact by collision between them and the granular adsorbent. Although moderate efficiencies may be obtained for very fine mists, the upper limit is generally in the range of molecular size.

*Gas Concentration*

As seen from the examination of adsorption isotherms, the quantity of gas adsorbed is a function of the gas concentration or pressure. An increase in concentration or pressure in the vicinity of the adsorbent results in an increase of the total amount of gas adsorbed.

*Presence of Other Gases*

Since the presence of additional gas molecules in a particular adsorbent-adsorbate system causes competition for the limited number of adsorption sites present, the observed effect is a reduction in the amount of adsorbate removed.

**Adsorbent Characteristics**

Most of the common adsorbents in use are more or less granular in form and are supported in a column through which the gas to be sampled is drawn. Common adsorbents have the capacity to adsorb 8 to 40% of their weight. An ideal adsorbent should be granular and of such size and form that it offers little or no resistance against flow. It should have a high adsorptive capacity; be inert and specific; be resistant to breakage, deterioration, and corrosion; be easily activated; and provide an easy release of adsorbate. Unfortunately, no one adsorbent possesses all these characteristics, so it becomes a matter of choosing the best adsorbent for a particular job.

*Surface Area*

All solids are capable of adsorbing gases to some extent. However, since adsorption is a surface phenomenon, it is not very pronounced unless the adsorbent possesses a large surface area for a given mass. For this reason, materials like silica gel and charcoals obtained from wood, bone, coconut shells, and lignite are very effective adsorbing agents. Since large surface areas are desirable for extensive adsorption, this factor is of primary importance in determining the amount of adsorbate that can be held by a unit of adsorbent. Solid adsorbents may vary in surface area from less than 1 to over 2000 square meters per gram. Typical approximate surface areas of several adsorbents are presented in Table 6-4. The latter two substances owe their high surface area to their porosity. They are thus capable of taking up large volumes of various gases.

**Table 6-4. Typical surface areas of adsorbents.**

Adsorbent	Area (m <sup>2</sup> /g)
Clay	5 – 15
Asbestos	10 – 20
Chalk	20 – 30
Carbon black	50 – 100
Silica or alumina gel	200 – 800
Activated carbon	500 – 2000

The extent of adsorption can be further increased by activating the adsorbents by various methods. For example, wood charcoal is activated by heating to between 350 and 1000°C in a vacuum, in air, in steam, and/or in the presence of other gases to a point where the adsorption of carbon tetrachloride at 24°C can be increased from 0.011 gram per gram of charcoal to 1.48 gram. The activation process involves distilling out various impurities from the adsorbent, thus leading to the formation of a larger free surface area for adsorption. Occasionally, large surface areas are produced by the original cellular



structure of the plant, as in the case of coconut shell charcoal. However, the activation process will increase the porosity of the material and may, under some circumstances, cause it to be less stable as an adsorbent. For example, if the temperature is raised, the porous structure of the adsorbent may aggregate into larger units that tend to become smooth and inactive. In many cases the past history of the adsorbent, with respect to preparation and method of activation, is just as important as the chemical characteristics in determining the adsorption capacity.

Often the adsorbent will exhibit an inherent preference for the adsorption of certain gases. This preference is primarily due to such factors as the method of preparation and activation, and the chemical nature of the adsorbent's surface. Preparation and activation methods not only may increase total adsorptive capacity, but they may also affect the adsorption process with respect to adsorbate size.

#### *Pore Size*

The pore size in the more porous adsorbents may vary in diameter from a few to several hundred angstrom units (1 angstrom [ $\text{\AA}$ ] =  $1 \times 10^{-10}$  meters). This may become a critical factor in selecting an adsorbent to remove a particular adsorbate. For example, iodine may be adsorbed on an adsorbent with a pore size of  $10 \text{ \AA}$  in diameter, while methylene blue is excluded by pores having a diameter less than about  $15 \text{ \AA}$ .

#### *Chemical Nature*

The chemical nature of the adsorbent's surface is an additional factor of considerable importance. It is of particular interest in chemical adsorption, where a rapid rate and a large degree of chemical reaction are desirable. In physical adsorption the nature of the surface is one of the primary factors influencing the strength of the adsorbent-adsorbate attraction. For example, a pure graphite surface physically adsorbs hydrophobic (i.e. water-hating) compounds to a large extent, while oxygenated surfaces are generally required to adsorb hydrophilic (i.e., water-loving) compounds appreciably at room temperature.

#### **Typical Adsorbents**

The various adsorbents used in physical adsorption may be classified according to their degree of polarity. For example, activated carbon, which is commonly known as a non-polar adsorbent, is largely composed of neutral atoms of a single species exhibiting little polarity. The non-polar adsorbents are most effective for gross decontamination of moist air streams containing materials of little polarity (e.g., organic molecules). The majority of the commercially important adsorbents other than carbon derivatives are simple or complex oxides. Their surfaces consist of heterogeneous distributions of charge on a molecular scale. They are strongly polar in nature. These adsorbents show a greater selectivity than do the carbon derivatives and exhibit a much stronger preference for polar than for non-polar molecules. In separation of various gases, the polar solvents are more useful than carbon derivatives. However, they are much less useful for overall

decontamination of moist air streams, since the strongly polar water molecules are preferentially adsorbed.

*Carbon*

Various forms of carbon serve as efficient adsorbents. It has been shown that the material from which the carbon is prepared has a demonstrable effect upon the ability of the carbon to adsorb various gases. Carbon prepared from logwood, for instance, has approximately twice the capacity for adsorption as carbon from rosewood. Similarly, coconut shell is about twice as efficient as logwood. Strangely enough the carbon prepared from harder, denser materials such as peach and other fruit pits, and coconut shells have the highest adsorptive capacities. Primary carbon is not nearly as efficient as activated carbon. The adsorbents “activated charcoal,” “active carbon,” “adsorbent carbon,” and “adsorbent charcoal” may be activated in a slightly different manner, but the terms are generally considered synonymous.

Activated carbon has a high adsorptive capacity, a high degree of hardness, high reliability, and other premium qualities. Almost all volatile materials, whether they are chemicals or mixtures of odor-causing substances, are retained within the microscopic porous structure to some extent. The only gaseous materials that it will not adsorb very well are low molecular weight gases such as oxygen, nitrogen, and carbon monoxide. Activated carbon finds its major application in solvent recovery and odor removal. It is also employed to a limited extent in the removal and monitoring of hydrogen sulfide, sulfur dioxide, and other toxic gases. Activated carbon is perhaps the most widely used adsorbent in air pollution control. The following substances are some of those that have been shown to be appreciably adsorbed upon activated carbon:

- |                      |                   |
|----------------------|-------------------|
| acetic acid          | iodine            |
| benzene              | carbon disulfide  |
| ethyl alcohol        | diethyl ether     |
| carbon tetrachloride | ammonia           |
| methyl alcohol       | hydrochloric acid |
| chloroform           | nitrous oxide     |
| acetone              | carbon dioxide    |
| acetaldehyde         | noble gases       |
| mercury vapor        | PVC               |

*Molecular Sieve*

Molecular sieve adsorbents<sup>3</sup> are synthetic sodium or calcium alumino-silicate zeolites of very high porosity. They are another representative of the siliceous adsorbents.

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<sup>3</sup> Often referred to as molecular sieve adsorbents.

The structural formula of a typical molecular sieve is  $\text{Me}_{z/n}(\text{AlO}_2)_y \cdot m\text{H}_2\text{O}$ , where Me represents exchange cations of charge  $n$ . The zeolite is precipitated as a white powder, bonded with clay, and formed into roughly spherical beads of four to twelve mesh size. The adsorbent is activated with heat to drive off water of hydration. The resulting product is a crystalline solid of very porous structure. Again, the adsorptive characteristics are dependent on the method of preparation.

Molecular sieves can be made very specific with respect to pore size. This characteristic gives them the outstanding property of being specific on the basis of adsorbate size and shape. Molecular sieves show a strong preference for the more polar molecules. For example, these adsorbents will not adsorb organic molecules that match their pore size from a moist stream of air, the accompanying water molecules being adsorbed in preference. Molecular sieves are truly selective adsorbents because they can separate mixtures on the basis of differences in molecular size, degree of polarity, and extent of carbon bond saturation. In addition to their selective properties, molecular sieves possess a high adsorptive capacity over wide ranges of concentration and temperature. They also are capable of removing impurities to extremely low concentrations. These adsorbents have been tested successfully on carbon dioxide, hydrogen sulfide, acetylene, ammonia, and sulfur dioxide. Unlike carbon, they can be used to effectively adsorb compounds of low molecular weight.

#### **Adsorption Losses in Air Sampling**

Each adsorption medium used in atmospheric sampling has different limitations and problems. The problems most frequently encountered are:

- irreversible adsorption,
- variable desorption efficiency, and
- interference by water vapor.

Activated carbon is used extensively because of its high affinity for organic substances. Irreversible adsorption and variable desorption efficiencies are two principal problem areas associated with carbon sampling devices. Carbon can also serve as a potent catalyst creating the possibility of *in situ* reactions during sampling.

Other alternative adsorption media that have recently been used extensively in air sampling are thermally stable, polystyrene divinyl benzene co-polymers. These media were used at ambient temperatures to collect volatile organic compounds. The volatile organic compounds were recovered by thermal desorption followed by gas chromatographic analysis. These polymers are non-polar and have little affinity for water. Water desorption represents a severe problem in the analysis procedure. Adsorption sampling devices are being used primarily for the collection of volatile organic compounds.

#### **Current Applications of Adsorption in Atmospheric Sampling**

Carbon, porous polymers such as Porapak Q, Porapak P, Tenax GC, XAD-resins, and polyurethane foam have been used extensively in collecting pesticides, polychlorinated biphenyls, and other organic compounds in ambient air. These

media can be used in sampling devices, which can be modifications of the hi-volume sampler (see Figure 6-5). Here polyurethane foam is used to collect organics, namely PCBs.

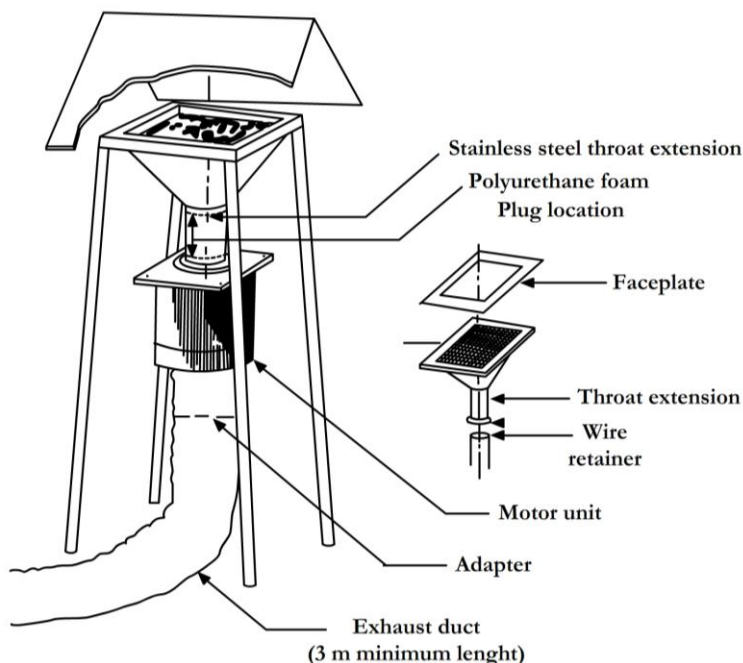


Figure 6-5. Assembled sampler and shelter with exploded view of the filter holder.

The details of this type of sampling effort can be found in Compendium Method TO-10A, Determination of Pesticides and Polychlorinated Biphenyls in Ambient Air Using Low Volume Polyurethane Foam (PUF) Sampling Followed by Gas Chromatographic/Multi-Detector Detection (GC/MD).

*Summary of Method TO-10A*

A low-volume sample (1-5 L/min) is pulled through a polyurethane foam (PUF) plug to trap organochlorine pesticides. After sampling, the plug is returned to the laboratory, and extracted and analyzed by GC coupled to multi-detectors (ECD, PID, FID, etc.).

Figure 6-6 illustrates an adsorbent sampling cartridge and Figure 6-7 shows a cartridge placed in a thermal desorption system. Figure 6-8 shows dynamic enrichment, which is repeated absorption from many different cartridges onto a single cartridge to attain enough of the species of interest for measurement.

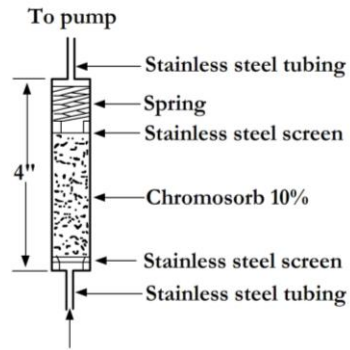


Figure 6-6. High-speed organic vapor collector.

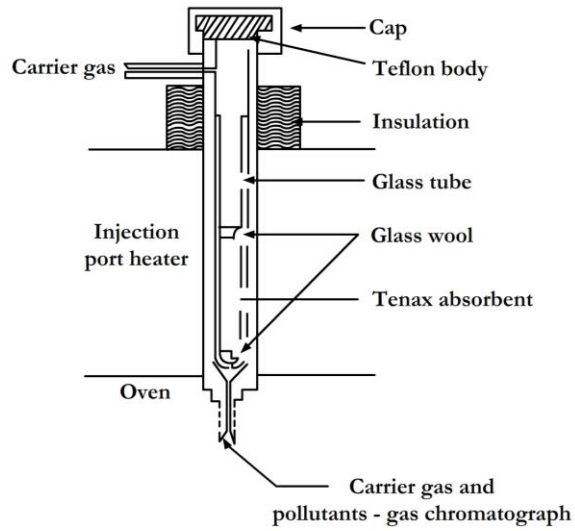


Figure 6-7. Desorption of pollutants from a Tenax-GC cartridge.

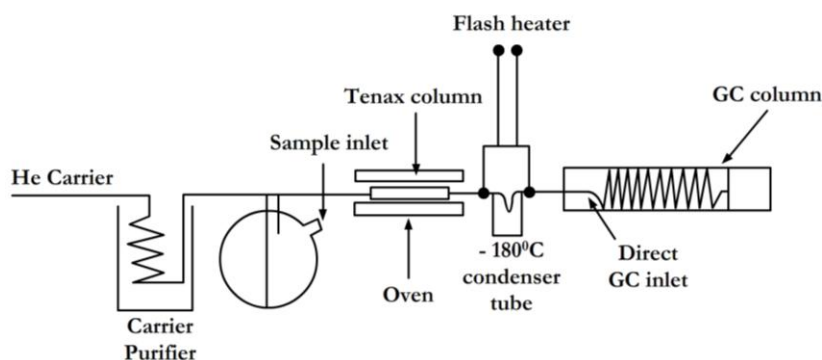


Figure 6-8. Dynamic enrichment on adsorption column (experimental setup).

Compendium Method TO-1, Method for the Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Tenax® Adsorption and Gas Chromatography/Mass Spectrometry (GC/MS) is an example of a sampling method which utilizes an adsorbent cartridge.

*Summary of Method TO-1*

Method TO-1 involves drawing ambient air through a cartridge containing ~1-2 grams of Tenax®. Selected VOCs are trapped on the resin, while highly volatile organic compounds and most inorganic atmospheric constituents pass through the cartridge. The cartridge is then transferred to the laboratory and analyzed. For analysis, the cartridge is placed in a heated chamber and purged with an inert gas, which transfers the VOCs from the cartridge onto a cold trap and subsequently onto the front of the GC column. The column is first held at low temperature (e.g., -70EC), then the column temperature is uniformly increased (temperature programmed). The components eluting from the column are identified and quantified by mass spectrometry.

**Summary**

The adsorption process is characterized by either physical or chemical forces. In some cases both types may be involved. Where physical forces predominate, the process is termed physical adsorption, whereas chemical adsorption describes chemical action.

Adsorption phenomena may be quantified by considering such adsorbate-adsorbent characteristics as gas composition, concentration, and temperature, as well as adsorbent type, surface area, and pore size.

## 6.5 Selection and Performance of Wet Collector Media

### Introduction

In the design of sampling trains, the most important component of the entire system is the collector. The process of pollutant removal is generally accomplished by absorption, adsorption, etc. The collector may take the form of a bubbler, impinger, etc. The process to be discussed is that of using a wet collector (absorber) for the collection of gases, vapors, and particulate matter. Some of the more important factors to consider are:

- solubility of pollutant,
- rate of reaction,
- collection efficiency, and
- retention characteristics of absorbant.

### Solubility of Pollutant

The solubility of a pollutant in a solvent must be considered in determining the type of absorber to choose. It will also determine the conditions under which the sample will be taken. The absorption coefficient is one method employed to express the results of solubility measurements with gases. The absorption coefficient  $\alpha$  is given by:

$$\text{(Eq. 6-7)} \quad \alpha = \frac{V_o}{(V)(p)}$$

Where:

- $V_o$  = the volume of gas dissolved (ml)
- $V$  = the volume of solvent (ml)
- $p$  = the partial pressure of the gas (atm)

Some typical absorption coefficients are given in Table 6-5.

Table 6-5. Absorption coefficient of gases at 20°C.\*

Solvent	H <sub>2</sub>	He	N <sub>2</sub>	O <sub>2</sub>	CO	CO <sub>2</sub>	NO	H <sub>2</sub> S	NH <sub>3</sub>
Water	.017	.009	.015	.028	.025	.88	.047	2.68	710
Carbon disulfide	.031	—	.049	—	.076	.83	—	—	—
Chloroform	—	—	.120	.205	.177	3.45	—	—	—
Ethyl alcohol	.080	.028	.130	.143	.177	3.0	—	—	—
Acetone	.065	.030	.129	.207	.198	6.5	—	—	—
Ethyl ether	.12	—	.24	.415	.38	5.0	—	—	—
Benzene	.066	.018	.104	.163	.153	—	—	—	—

\*Glasstone S. 1946. Textbook of physical chemistry. New York: D. Van Nostrand, p. 695.

*Influence of Temperature*

When gases dissolve in a liquid, there is generally liberation of heat; it follows, therefore, that an increase of temperature will result in a decrease of solubility. It is for this reason that gases may be readily expelled from solution by boiling. By thermodynamic methods, it is possible to show that an increase in temperature will decrease the solubility of a gas. This effect can be seen in Table 6-6.

Table 6-6. Influence of temperature on solubilities of gases in water.\*

Gas/temp	Helium	Nitrogen	Oxygen	Carbon Dioxide
0°C	.0094	.0235	.0489	1.713
30°C	.0081	.0134	.0261	.665

\*Glasstone 1946, p. 696.

*Influence of Pressure*

The most important factor influencing the solubility of a gas is pressure; increasing the pressure of the gas will tend to increase its solubility. The pressure is expressed by Henry's law, which states that the mass of a gas dissolved by a given volume of solvent, at constant temperature, is proportional to the pressure of the gas with which it is in equilibrium.

(Eq. 6-9) 
$$m = kp$$

Where:  $m$  = mass of gas dissolved by unit volume of solvent (g)  
 $p$  = equilibrium pressure (atm)  
 $k$  = constant



Some examples of pressure versus solubility effects are given in Table 6-7.

Table 6-7. Influence of pressure on solubility of CO<sub>2</sub> in various solvents at 59°C.\*

Solvent/pressure	Methyl alcohol	Acetone	Methyl acetate
100 mm	42.5	67.2	75.8
200 mm	42.7	68.0	77.1
400 mm	43.1	69.2	77.6
700 mm	43.3	72.8	79.0

\*Glasstone 1946, p. 697.

### Rate of Reaction

All chemical reactions take place at a definite rate, depending on process conditions. The most important factors are concentration of reactants, temperature, and presence of a catalyst or inhibitor. Some reactions are so rapid that they appear to be instantaneous, whereas others are so slow at ordinary temperatures that no detectable change would be observed in the course of years. Between these two extremes are many processes taking place with measurable velocities at temperatures easily accessible in the laboratory.

Since the rate of a reaction is proportional to the concentration of the reacting substances, it is evident that the rate of the process must fall off as the reaction proceeds. This phenomenon can, however, be used to advantage by increasing the concentration of the absorbing liquid, thereby forcing the reaction to approach completion rapidly.

### Collection Efficiency

There are three major factors inherent in the design of a bubbler that can affect the efficiency of the absorber: bubble size, flow rate, and height of liquid column.

#### *Bubble Size*

The surface area at the gas-liquid interface is inversely related to the average volume of the gas bubble. As the volume of individual bubbles decreases, the surface area at the gas-liquid interface increases.

The efficiency of absorption of a gas or vapor by chemical reaction or physical absorption depends on the probability of successful collisions with molecules of reagent or solvent at the gas-liquid interface. For a given concentration of reagent this will depend on the surface area of the gas bubbles, on the length of the column of liquid through which the bubbles must pass, and the rate at which they rise through the liquid.

Collection efficiency varies inversely with flow rate and bubble size, and varies directly with the height of the liquid column.

#### *Flow Rate*

The gas flow rate through an absorber is one of the factors determining the efficiency of an absorber. Figure 6-9 shows clearly that as flow rate increases, for the absorbers

studied, the efficiency decreases. This efficiency versus flow rate curve should be determined for each absorber and used in any analysis, as required by the method.

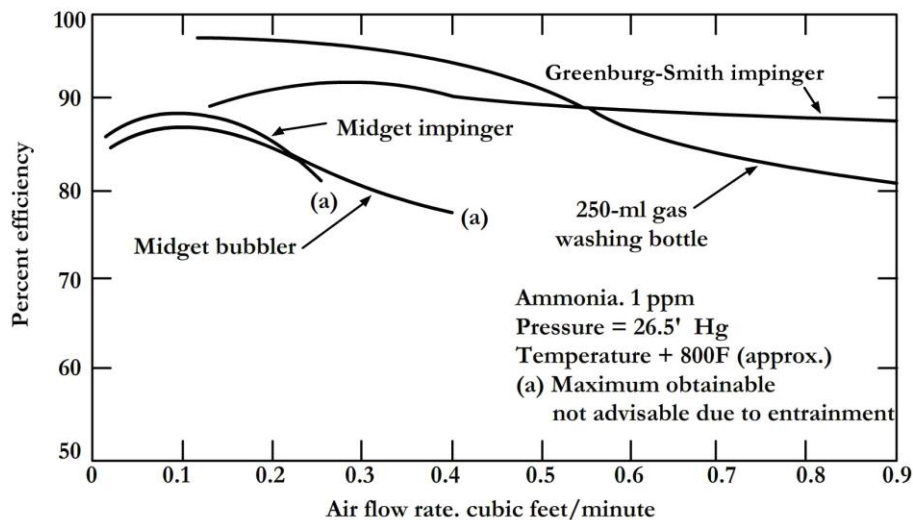


Figure 6-9. Performance curves - commercially available absorbers.

*Height of Liquid Column*

The length of the column of liquid in an absorber is important in determining efficiency. The velocity of rise of bubbles is approximately constant at 24 cm/sec for bubble diameters greater than 0.2 cm. Since the bubbles rise at approximately 24 cm/sec, they will be in contact with a liquid column 24 cm long for 1 second, 48 cm long for 2 seconds, etc. The longer the gas bubble is in contact with the liquid, the more pollutant is transferred from the gas phase to the liquid phase until gas-liquid equilibrium is approached.

**Retention Characteristics of Absorbent (Solvent)**

The equation defining Raoult's law is:

(Eq. 6-10) 
$$p = Np_0$$

Where:  $p$  = partial pressure of gas to be dissolved (atm)  
 $N$  = mole fraction of gas  
 $p_0$  = vapor pressure of gas (atm)

From this relationship one can calculate the solubility of a gas below its critical temperature, on the assumption that the solution behaves in an ideal manner. For example, the critical temperature of ethane is 34°C. At 25 °C the pure liquid has a vapor pressure of 42 atm. According to Raoult's law, therefore, the solubility of ethane at 25°C and a pressure of 1 atm in any solvent in mole fraction can be determined by the following:

$$N = \frac{p}{p_0} = \frac{1}{42} = 0.024$$

since  $p$  is 1 atm and  $p_0$  is 42 atm. The actual solubility in n-hexane at 25°C and 1 atm pressure is 0.017 mole fraction. This variation is due to n-hexane being a non-ideal solvent.

To extend the method for calculating gaseous solubilities to temperatures above the critical temperature, it is necessary to estimate the hypothetical vapor pressure of the liquid by a suitable extrapolation. This is best done by using the integrated form of the Clapeyron-Clausius equation, which is:

$$\text{(Eq. 6-11)} \quad \log \frac{p_2}{p_1} = \frac{L_{\bullet}}{4.576} \left[ \frac{T_2 - T_1}{T_2 T_1} \right]$$

Where:  $L_{\bullet}$  = latent heat of vaporization

If the vapor pressure at any two temperatures is known, the value at any other temperature may be evaluated on the assumption that the molar heat of vaporation remains constant. The critical temperature of methane is 95.5°C, and the hypothetical vapor pressure of the liquid at 20°C is 310 atm, giving an ideal solubility at this temperature and a pressure of 1 atm of  $1/310 = 0.0032$  mole fraction: this is very close to the solubilities actually found in n-hexane and m-xylene. Since the solubility in mole fractions of a gas at 1 atm pressure is equal to  $1/p$ , where  $p$  is the vapor pressure of the liquified gas, it is evident that, for ideal solutions, the lower the vapor pressure at the given temperature, the greater will be the solubility of the gas. Gases that are liquified only with difficulty, that is to say, those having very low boiling points, may be regarded as having high vapor pressures; such gases will, therefore, have low solubilities. It follows that, in general, easily liquifiable gases will be the most soluble; this is in agreement with observation in most cases.

Although the solubility of a gas, in mole fractions, should theoretically be independent of the nature of the solvent, this is not true in practice because of departure from ideal behavior. Some data for solutions of gases showing deviations are listed in Table 6-8. The solubilities in water are exceptionally low; since water is both polar and associated, and also has a very high internal pressure, solutions of gases of the type mentioned would hardly be expected to behave ideally. Even chlorine and carbon dioxide, which interact with water and are generally regarded as relatively soluble gases, have solubilities considerably below the calculated values, because of their low polarity and internal pressure. A quite different type of behavior is shown by ammonia, which is a highly polar substance with a high internal pressure. In hydrocarbon solvents, therefore, solubility is considerably below the ideal value, whereas in alcohol and water the observed solubility is somewhat greater than that calculated. If allowance could be made for interaction between ammonia and the solvent, good agreement would be found. A corollary to the foregoing conclusions is that for a number of gases of similar polarity and internal pressures (e.g., hydrogen, nitrogen, carbon

monoxide, oxygen) that do not react with the solvent, the ratio of the solubilities in various solvents should be approximately independent of the nature of the gas. This generalization is roughly true in practice, and only gases such as carbon dioxide and ammonia, which are not in the same category, are exceptions.

Table 6-8. Ideal and observed solubilities at 20°C.

Gas	Ideal	Nitrobenzene	Ethyl alcohol	Aniline	Water
Nitrogen	10	2.6	3.3	1.1	0.13
Carbon dioxide	11	3.9	4.5	1.9	0.19
Oxygen	16				0.17
Argon	21		6.5		0.17

### Retention of Gases and Vapor by Chemical Reaction

The usual objective in the selection of an absorbent for scrubbing a gas is to find a liquid, possibly a solution, with a very large capacity for absorbing the solute without building up an appreciable equilibrium back pressure. This can be accomplished readily by choosing a chemical with which the solute reacts irreversibly, as when an aqueous solution of sodium hydroxide is used to absorb carbon dioxide. There are indeed very few absorptions of a gas in a liquid that are not accompanied by a chemical reaction to some degree. Thus, when ammonia dissolves in water, ionization occurs that may be looked upon as a chemical change. A similar phenomenon, though potentially weaker, occurs when carbon dioxide dissolves in water. A much stronger and more definite chemical change takes place when ammonia is dissolved in an acid, or carbon dioxide in a base.

There is no sharp line dividing pure physical absorption from absorption controlled by the rate of a chemical reaction. Most cases fall in the intermediate range, the rate of absorption being limited both by resistance to diffusion and by the finite rate of reaction. Simultaneous occurrence of a chemical reaction renders the mechanism of absorption more complicated. The theory of purely physical absorption rests on the assumption of the two-film concept. This theory may be carried over to the case where a simultaneous reaction occurs; however, modification in film resistance will become apparent. Thus, when carbon dioxide is dissolved in water, the rate-controlling factor is not the migration of the dissolved carbon dioxide from the liquid surface into the liquid interior, simply because the rate of solution of the gas in water is small from the very start. On the other hand, if absorption of carbon dioxide in a solution of sodium hydroxide is considered, the rate of absorption is very rapid, and the rate of migration of the carbonate into the main body of the liquid becomes rate-controlling.

These phenomena are complex and, although considerable advances have been made, the situation is still very obscure. Whenever there is a pronounced chemical reaction occurring simultaneously with absorption, there are essentially two effects that must be considered:

- modification of capacity (rate) data, and
- modification of the driving force.

Capacity coefficients will generally, but not always, increase when a chemical reaction occurs simultaneously with absorption. At present there is no data available to permit a correlation that will allow for estimation of capacity data.

As far as driving force is concerned, an increase is usually observed as a consequence of a chemical reaction. In many cases the dissolved gas, once having reacted with a constituent in the liquid, offers virtually no resistance to further absorption. This is the case when carbon dioxide or sulfur dioxide is dissolved in basic solutions.

### **Retention of Particulate Matter**

The design of the absorber plays a most important part in the retention of particulate matter by a liquid. A liquid absorber is highly efficient for retaining particles only when the velocity of the air at the jet approaches that of sound and the particles impinge with high velocity on a surface in the liquid. The sudden change in kinetic energy results in the virtually complete trapping of all particles having a diameter greater than 1 micrometer.

## **6.6 Principles of Grab Sampling**

### **Introduction**

The term “grab sample” suggests two concepts: (a) a sample taken at a particular time and place within an interval of a few seconds to a minute or two, and (b) a small representative portion removed from the gross sample with no alteration. Since there is no alteration to the sample, such as occurs when the pollutant is separated from the gas stream by sorption for instance, grab sampling is often referred to as “Whole Air Sampling.” When a series of grab samples are combined or when a grab sample is conducted at a low sample flow rate over an extended period of time, up to 24-48 hours, the sample is said to be an integrated sample (i.e. integrated sampling).

Grab samples are usually collected in one of the following ways:

- using an evacuated container,
- purging (displacement of air),
- displacement of a liquid,
- inflation of a plastic bag, or
- using a syringe.

### **Evacuated Containers**

Evacuated containers used for grab sampling are of several types, which include:

1. stainless steel canisters,
2. vacuum tubes (glass), and
3. vacuum flasks (glass).

*Stainless Steel Canisters*

These canisters are often referred to as SUMMA canisters due to the “Summa” process used to passivate the internal surface to make it chemically inert. A Summa surface has the appearance of a mirror, bright and shiny. Summa canisters typically range in volume from 1 liter to 15 liters. Six-liter canisters are generally used for ambient air samples and for collecting samples over time.

A sample enters a canister through a high temperature stainless steel bellows valve. A Summa canister will hold a high vacuum (>28" Hg) for up to 30 days. Beyond 30 days, low level concentrations of typical VOCs may be present resulting in erroneous ambient air data.

Stainless steel canisters are the “work horses” of grab and integrated sampling and have displaced the use of most other devices, except for inflation of plastic bags (discussed later in this section).

**Sampling with Canisters**

1. Verify Initial Vacuum of the Canister (typical for Air Toxics LTD Canisters):
  - a. Confirm the valve is closed.
  - b. Remove the brass cap.
  - c. Attach pressure gauge and cap side fitting with brass cap.
  - d. Open and close valve quickly (a few seconds).
  - e. Read vacuum on the gauge & record on data sheet.
2. Grab Sample Procedure (typical):
  - a. Confirm valve is closed.
  - b. Remove brass cap.
  - c. Attach particulate filter to canister.
  - d. Open valve ½ turn (6 L canister usually takes about 16 secs to fill).\*
  - e. Close valve.
  - f. Verify and record final vacuum (repeat steps for initial vacuum verification).
  - g. Replace brass cap.
  - h. Ensure Chain of Custody documents are completed.
  - i. Send canister for analysis.

\*Note: A grab sampling can be collected either by allowing the canister to reach ambient conditions (not typical) or by leaving some residual vacuum (e.g. 5 in. Hg) in the canister. In either case the final vacuum must be noted on the Chain of Custody data sheet. This will enable the laboratory to compare the final vacuum with the vacuum recorded at the end of the sampling period to determine if the canister “seal” was compromised.

Integrated sampling is accomplished by introducing a flow restriction device at the inlet of the canister. The most common flow restrictors used are mass flow controllers and critical orifice devices. Both devices are driven by differential pressure between ambient conditions and the vacuum in the canister.

**Precautions for Integrated Sampling with Canisters.** Collecting an integrated sample is more complicated than when collecting a grab sample. Sampling precautions include verifying that the sampling train is properly configured, monitoring the sampling progress, and avoiding contamination.

- *Avoid Leaks in the Sampling Train.* A leak in any of the connections can mean that some of the air will be pulled in through the leak and not through the flow controller. A final pressure reading (vacuum) less than expected at the end of the sampling period is an indication that there may have been a leak.
- *Monitor Sampling Progress.* The volume of air sampled is a linear function of the canister volume. For example, halfway (4 hours) into an 8-hour sampling period, the canister should be half-filled (2.5 L) and the gauge should read approximately 17 in. Hg. A vacuum reading greater than 17 in. Hg (>17) indicates the canister is filling too slowly; less than 17 in. Hg (<17) and the canister is filling too quickly.
- *Avoid Contamination.* Flow controllers must be cleaned between uses. This is conducted in the laboratory; not in the field.
- *Caution Against Sampling in Extreme Temperatures.* There can be some flow rate drift if the temperature of the controllers varies appreciably. This is of particular concern for the mass flow controllers.

*Vacuum Tube*

One common type is a strong glass tube of 250 to 300 ml capacity, although tubes with volumes as large as 1 to 2 liters are sometimes used (Figure 6-10).

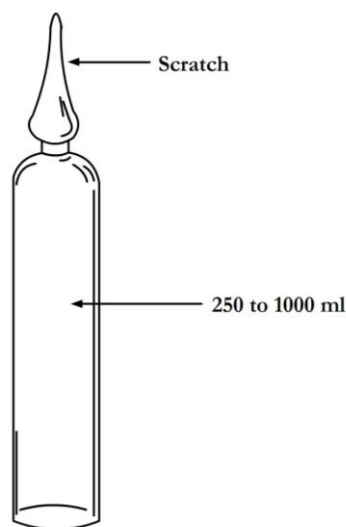


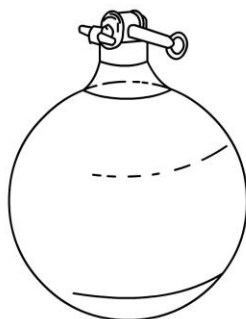
Figure 6-10. Vacuum tube.

To use this type of container, the tube is evacuated until almost all the air has been removed. In the last stages of evacuation, the neck is sealed. Then at the sampling site, the neck is scratched and broken. Sampling is instantaneous, and will continue until the internal pressure is equivalent to the external pressure. The broken end is then sealed with wax and sent to the lab for analysis.

There are several advantages in the use of this collector: it is simple to use and no pump or manometer need be taken to the sampling site. However, the tube must be redrawn, re-evacuated, and resealed if it is to be used again. There is also the danger of breakage. Vacuum tubes are rarely, if ever, used today.

*Evacuated Flask*

An evacuated flask fitted with a stopcock or vacuum cap can also be used in this type of sampling (Figure 6-11). The flask is evacuated and then sealed by giving the cap a half turn. When sampling is to occur, the cap is turned to the “open” position and the air will be drawn into the flask. The cap is closed after sampling and the flask is returned to the laboratory.



**Figure 6-11. Vacuum flask.**

During the transport of the evacuated container to the sampling site there is a possibility of slow leakage through poorly fitted stopcocks. This would, of course, completely invalidate the results. The pollutants to be analyzed may also degrade or react with other compounds in the evacuated flask. This apparatus has the advantage of being easy to reuse. Such collectors should be placed in a protective container or wrapped with adhesive tape to reduce hazards of implosion.

If for some reason the containers are not completely evacuated, it may be necessary to subtract a residual volume from the volume of the flask to determine the volume of air sampled. Let  $V_f$  be the volume of the vessel; after evacuation let the temperature and residual pressure in the flask be  $T_1$  and  $P_1$ .



The flask is transported to the sampling site and opened; the flask temperature and pressure now become  $T_2$  and  $P_2$ . The volume of air sampled,  $V_2$ , is given by:

$$\text{(Eq. 6-12)} \quad V_2 = V_f - V_z$$

where  $V_z$  is the volume occupied by the residual gas. Assuming gas ideality for the residual gas:

$$\text{(Eq. 6-13)} \quad \frac{P_2 V_z}{T_2} = \frac{P_1 V_f}{T_1}$$

Hence:

$$V_z = V_f \left( 1 - \frac{P_1 T_2}{P_2 T_1} \right)$$

If the ratio  $P_1/P_2$  is small (almost complete evacuation), then the correction can be neglected and

$$V_z = V_f$$

The presence of the pollutant in the residual gas would further complicate the matter. Vacuum flasks are rarely, if ever, used today.

**Air Displacement or Purging**

Cylindrical tubes with stopcocks at each end are used as collectors (Figure 6-12). The stopcocks are opened and the tube is thoroughly purged. After sampling, the tube should be held in place until the stopcocks have been closed and the aspirating device has been removed.

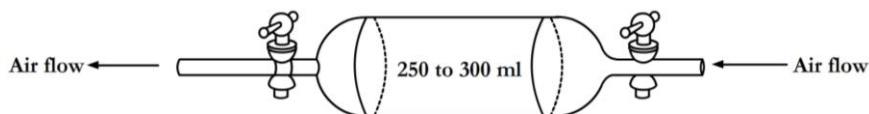


Figure 6-12. Gas-displacement collector.

Metal containers of the same general design have been employed, but they have been found to react with many samples. Their real advantage lies in the fact that they are virtually unbreakable.

The sample air is drawn through the container using any of a variety of pumps. Enough air must be drawn through to completely flush out old, unrepresentative air that may be present.

The necessary volume of air required will vary, but in all cases it will be at least several times greater than the volume of the container. Theoretically all of the old air can never be eliminated by pumping. Since this pumping process may take a relatively long time, it is not strictly an instantaneous sample. If the

concentration of pollutant in the air changes radically during purging, the results will not necessarily be close to the average over the time interval involved.

**Liquid Displacement**

Another technique used in gas sampling is liquid displacement. In this method a liquid is allowed to drain from the bottom of a container, while an opening at the top allows the gas to enter and fill the space left by the liquid. Any suitable liquid that will not dissolve the sample nor react with it can be used. The choice of liquid will depend upon the material being sampled; some commonly used liquids are water, brine, mercury, or water saturated with the gas to be sampled.

Containers used are of two basic types: (a) a glass tube with two stopcocks as used in air displacement (Figure 6-13) and (b) an aspirator bottle (Figure 6-14).

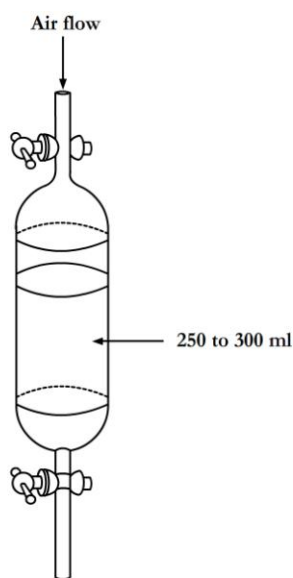


Figure 6-13. Liquid-displacement collector.



Figure 6-14. Aspirator bottle.

In both cases, the liquid is allowed to drain through the lower opening (the rate can be controlled by adjusting the stopcock), and the gas is drawn in through the upper stopcock or tube. This method requires a minimum of equipment and no special training. The container may be calibrated to indicate the volume of gas sampled. Gas- and liquid-displacement as ambient air sampling methods are rarely, if ever, used today.

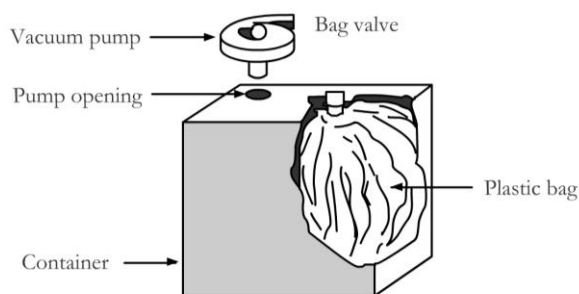
**Inflation—Plastic Bag Sampling**

A fourth gas sampling method is the collection of a sample by inflation of a plastic bag. Plastics of various types have been used. The choice of material will

depend on the gas to be sampled and the storage period. This method of grab or integrated sampling remains in use today, particularly in saturation studies where numerous samples are needed and a high degree of accuracy is not required.

Some hazards to look out for in “bag sampling” are wall effects, memory effects (where previous constituents linger), sample deterioration over time, sample deterioration due to sunlight in some cases, and the possibility of reactions among the various gases in the bag.

The deflated plastic bag is placed in a closed, air-tight box, with only a tube extending outside the box. An opening in the box itself is connected to a vacuum source, and the air is pumped out of the box. As the air is removed from the outer container, the bag will inflate, drawing in the sample. The air may be metered as it is pumped out of the box, thus indicating the volume of gas sample drawn into the bag (Figure 6-15). The inflation sampler is sometimes referred to as a “lung sampler,” since it mimics how the human lung is inflated.



**Figure 6-15. Inflation sampler.**

**Table 6-9. Comparison of canisters and plastic (Tedlar) bags.**

	<b>Canisters</b>	<b>Tedlar Bags</b>
<b>Common Volumes</b>	1 and 6 L	1, 3, and 5 L
<b>Type of Sampling</b>	Passive (vacuum)	Active (pump required in field)
<b>Sample Handling</b>	Room Temperature	Room Temperature
<b>Media Hold Time</b>	Up to 30 days	Indefinite
<b>Hold Time to Analysis</b>	Up to 30 days	Up to 3 days
<b>Surface Inertness</b>	Excellent	Fair
<b>Cleanliness</b>	Certified to ppbv/pptv levels	Some VOC's present at 0.5 to 45 ppbv

<b>Sampling Applications</b>	Ambient/indoor air, soil/landfill gas, stationary sources	Ambient/indoor air, soil/landfill gas, stationary sources
<b>“Sensitivity”</b>	“ppbv device”	“ppmv device”
<b>Advantages</b>	Inertness, hold time, ruggedness, no pump needed in field	Purchase/shipping cost, availability, convenience

**Syringes**

Syringes may be used in the collection of small gas samples. This technique has been widely applied in the field of odor measurement.

**Grab Sampling Techniques**

Grab sampling techniques are preferable to continuous sampling in certain situations. Some constituents have absorption rates too slow for efficient collection by absorption. Field conditions (lack of electricity and lab facilities) often necessitate this type of sampling.

Grab sampling is useful when concentrations vary considerably over a period of time, and it is necessary to obtain a sample at a specific time. Most grab sampling techniques utilize a minimum of equipment and require little or no special training or experience on the part of the operator.

Grab sampling has a serious limitation – the sample obtained is generally not large enough to detect very small quantities of materials except by the most sensitive techniques.

**Current Applications of “Whole Air” (Grab and Integrated) Sampling in Ambient Air**

*Summary of Compendium Method TO-14A: Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Specially Prepared Canisters with Subsequent Analysis by Gas Chromatography*

Whole air samples are collected in an evacuated stainless steel canister. VOCs are concentrated in the laboratory with cryogen trap. VOCs are revolatilized, separated on a GC column, and passed to one or more detectors for identification and quantitation.

**6.7 Principles of Cryogenic (Freezeout) Sampling**

**Introduction**

Air pollutants existing as gases can be trapped or removed by the freezeout, or condensation, method. Trapping in this discussion refers to the mechanism of sample collection, and removed implies an air-cleaning mechanism to separate

gas contaminants from the gas stream. The method has a very high efficiency at relatively low flow rates.

**Concept**

The method consists essentially of drawing air through collection chambers with progressively lower temperatures. If the temperatures of the chambers are approximately equal to or less than the boiling point (the temperature at which a liquid is converted to a gas) of the gaseous components of the air passing through it, these components will exhibit a phase change from the gaseous phase to the liquid phase. The condensate (liquid phase) is collected in the chamber where the phase change occurs. The gaseous contaminants to be collected will determine the temperatures required in the collection chambers. The temperatures of the chambers can be controlled by using different immersion bath liquids. Contaminants with boiling points as low as  $-195^{\circ}\text{C}$  can be collected by this method.

**Equipment**

The type of freezeout equipment required depends to a large extent on the application. The required amount of equipment of a given type depends on whether the sampling apparatus is a single or multistage unit.

The size of the collection chamber varies according to the immersion bath for which it was designed. The collection chambers themselves are placed in Dewar flasks containing the cooling solutions (Figure 6-16).

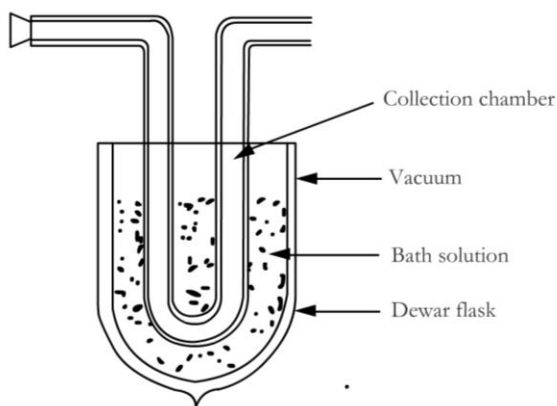


Figure 6-16. Freezeout unit.

Table 6-9 indicates various bath solutions and some sizes of the Dewar flasks that have been used for each. The volume of the bath solutions and, thus, the size of the collecting chamber itself are partially due to factors such as:

- temperature gradients across the collecting chambers as related to the criticality of the boiling point of the contaminant being collected,
- the surface area as related to the evaporation rate of the bath solution, and

- the condensation of water vapor in the primary collection chambers, thus necessitating a larger volume.

Table 6-9. Bath solutions.

Bath solution	Temperature	Volume of solution
Ice & salt	- 16°C	≈ 2 liter
Dry ice & acetone or methyl-cellosolve	-80°C	750 ml
Liquid air	147 °C	100 ml
Liquid oxygen	-183°C	100 ml
Liquid nitrogen	-195°C	100 ml

The level of the solutions in the baths should be kept at 2” to 4” within the top of the collection chambers in an attempt to maintain a constant temperature throughout the chamber.

Among the collection chambers utilized, U-shaped and spiral-shaped tubes are prominent. Large radius bends should be designed into the tubes to facilitate smooth airflow and to prevent ice accumulation at the bends. Freezeout devices can be classified into two categories: single-stage and multistage units.

**Single-Stage Units**

A single-stage unit (Figure 6-16) consists of one collection chamber (glass or metal) immersed in a bath solution. As has already been mentioned, the temperature of the bath and, consequently, the liquid of the bath will depend on the particular gas to be sampled.

**Multistage Units**

Multistage units consist of a series of collection chambers. These chambers can be arranged in either horizontal or vertical trains (Figures 6-17 and 6-18). In these trains the temperatures of the baths are progressively lower. This allows for condensation of different gases in different chambers.

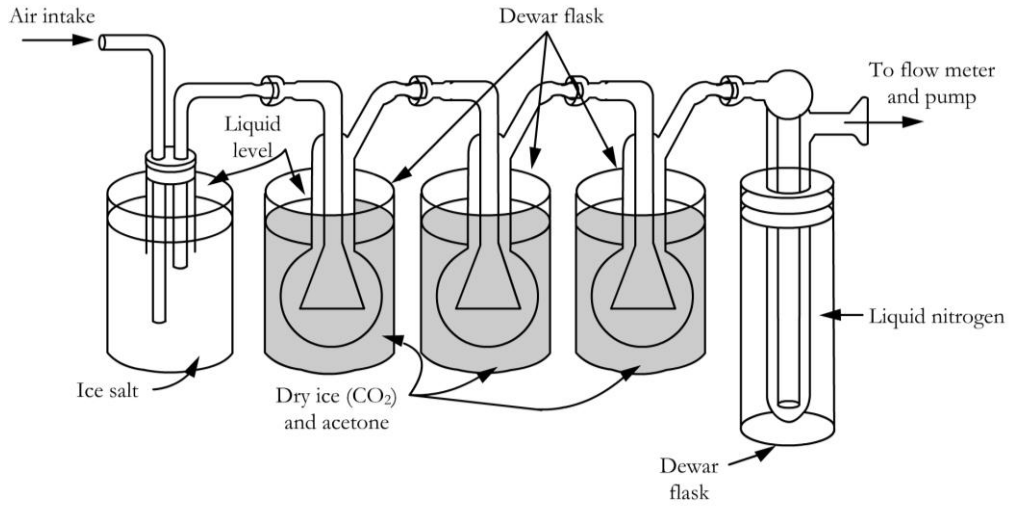


Figure 6-17. Freezeout equipment for atmospheric sample (horizontal sampling train).

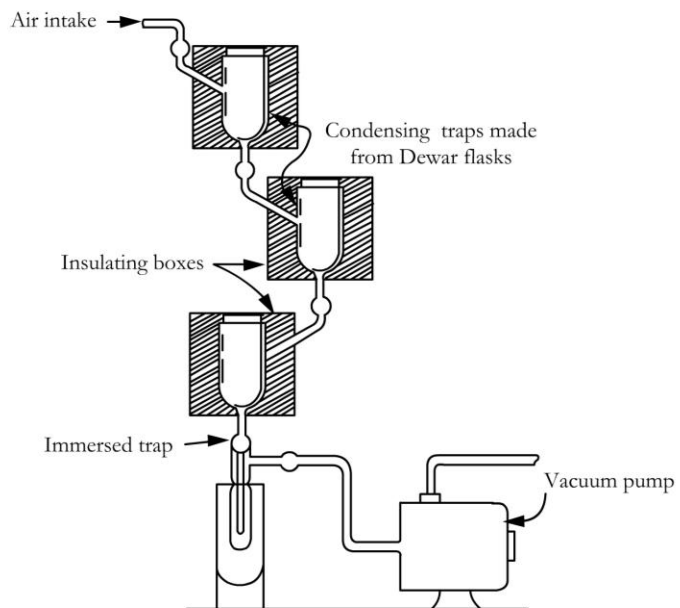


Figure 6-18. Freezeout equipment for atmospheric samples (vertical sampling train).

### Efficiency

The collection efficiencies of the previously described systems are not very good. To efficiently condense gases it is necessary for the gas to come in contact with the cold surface of the collection chamber. Therefore, the efficiency of collection by freezeout can be improved by: (a) filling the collection chamber with some type of material that will increase the cold surface area and (b) reducing the flow rate.

### Packing Materials

To increase the cold surface area within the collection chamber, various materials such as glass beads, metal packing, and activated carbon have been used (Figure 6-19). In one application, for collecting benzene and formaldehyde, the glass beads and metal packing increased the efficiency from 50% to 65% and 60%, respectively. The lower collection efficiency of the unpacked train was due partly to the formation of a fine mist that was not retained by the walls of the traps.

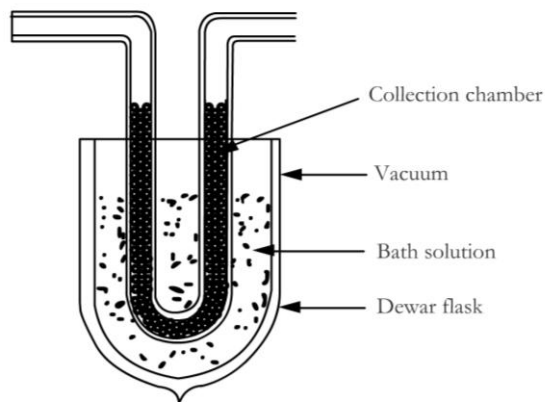


Figure 6-19. Freezeout unit showing packing material.

In another application using activated carbon, a collection efficiency of 100% was reported for xenon and krypton. The activated carbon gave a much larger surface area for the gas to pass over. The use of activated carbon will give the added advantage of adsorbing gases from the air stream.

### Flow Rate

The flow rate through the train should be such that a sufficient “detention time” (time allowed for the gas to come into equilibrium with its surrounding temperature) is available to allow the desired collection efficiency. For an unpacked train the detention time must be relatively large due to the small, cold surface area. By packing the train with a surface-area-increasing material, the cold surface area will increase and the detention time can become smaller. With a smaller required detention time, the rate of flow through the train can be greater. Flow rates on the order of 0.1 to 0.2 cfm have been reported for unpacked trains, while 1 to 2 cfm has been reported for trains packed with activated carbon.



Another factor affecting flow rate is the formation of ice crystals in the bends of the collection chambers. This will be discussed in another section.

#### *Errors*

One possible source of error is that gases soluble in water will be removed to some extent prior to their removal in a collection chamber. Other errors may be introduced when electrostatic precipitators, drying towers, etc., are placed ahead of the freezeout train. Electrostatic precipitators will aid in the removal of particulate matter, but they may also alter the gas chemically. Adsorption of vapors by a desiccant placed before the collection chamber has also been reported. This adsorption might introduce errors in the final results.

#### *Sensitivity*

The sensitivity of the freezeout method depends primarily on the gas collected, volume of air sampled, and how the collected gas is analyzed. Hydrocarbon samples were analyzed on a mass spectrometer to detect pollutant concentrations of  $10^{-4}$  ppm from a 1-liter sample. With larger sample volumes, concentrations on the order of  $10^{-6}$  ppm have been reported.

#### *Freezeout Train*

Trains composed of several collection chambers have the ability of collecting several gases at the same time. This may aid in the gross analysis of the sample because the sample will be broken into fractional parts according to the various boiling points of the gases.

Probably the main disadvantage of a freezeout train is the plugging of the collection chambers by ice crystals. Drying towers placed on the inlet side of the train will help alleviate this problem as well as filter some particulate matter. Flow rates of 1 to 2 cfm have been reported when using a drying tower.

Liquid oxygen creates another problem when it is used as a bath solution or when collected in a collection chamber. When used as a bath solution, extreme care must be employed because of the ability of liquid oxygen to support combustion. Therefore, a restricted personnel area around the sampler must be maintained. Oxygen (B.P. =  $-183^{\circ}\text{C}$ ) will condense when liquid nitrogen (B.P. =  $-196^{\circ}\text{C}$ ) is used as a bath solution. This is undesirable since it will dilute the collected contaminants. If the solution is allowed to warm up after sampling, a portion of the contaminants may be carried off by the escaping oxygen.

#### *Multicollection Train*

The freezeout train may be part of a larger train where particulate matter filters, electrostatic precipitators, activated charcoal cartridges, etc., make up the rest of the train. The major advantage of such a train would be the removal of particles and gases that were not of interest. Probably the main disadvantage of the larger train is the possibility of altering the chemical composition of the gas of interest.

#### **Current Applications of Cryogenic "Freezeout" Sampling in Ambient Air**

The freezeout method has proved useful in sampling gases. The freezeout device can be used as a collecting train itself, or it can be used in conjunction with other

sample collection devices. Also, freezeout traps are used in the lab to concentrate trace amounts of pollutants (such as halogenated hydrocarbons) desorbed from adsorption cartridges in order to increase their detectibilities. This probably is its chief use today.

*Summary of Compendium Method TO-3: Method for the Determination of Volatile Organic Compounds in Ambient Air Using Cryogenic Preconcentration Techniques and Gas Chromatography with Flame Ionization and Electron Capture Detection*

Method TO-3 involves the *in situ* collection of VOCs having boiling points in the range of -10°C to 200°C in a cryogenic trap constructed of copper tubing packed with glass beads. The collection trap is submerged in either liquid nitrogen or liquid argon. Liquid argon is highly recommended because of the safety hazard associated with liquid oxygen. With the sampling valve in the fill position, an air sample is admitted into the trap by a volume measuring apparatus. In the meantime, a GC column oven is cooled to a subambient temperature (-50°C) for sample analysis. Once sample collection is completed, the valve is switched so that the carrier gas sweeps the VOCs in the trap onto the head of the cooled GC column. Simultaneously, the liquid cryogen is removed, and the trap is heated to assist the sample transfer process. The GC column is temperature programmed, and the component peaks eluting from the columns are identified and quantified using flame ionization and/or electron capture detection. Alternative detectors (e.g., photoionization) can be used as appropriate. An automated system incorporating these various operations as well as the data processing function is described in the method. Due to the complexity of ambient air samples, high resolution (capillary column) GC techniques are recommended.

**Summary**

Freezeout trains have proved to be an efficient collection device. Collection efficiencies of 100% for flow rates up to 2 cfm have been reported for certain contaminants. Problems such as water vapor condensation with subsequent plugging of collecting chambers can be alleviated by using a desiccant on the inlet side of the train. Collection efficiency improvements such as increasing the cold surface area can be accomplished by using a packing material. The use of freezeout devices for “field” operations has its limitations because of its bulkiness and the problem of keeping the bath solutions at a constant level.

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