Chapter 4

Particle and Gas Phase Interactions in Air Sampling

Sidney C. Soderholm, Ph.D.
National Institute for Occupational Safety and Health, Morgantown, West Virginia

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CONTENTS

Introduction

An aerosol consists of airborne particles and surrounding gases. The particle phase may include solids and liquids. The gas phase normally includes air and water vapor and may include vapors of organic and inorganic compounds as well as contaminant gases, such as sulfur dioxide. The distinction between a vapor and a gas is somewhat arbitrary. Following common practice, the term "vapor" refers to the gas phase portion of a material which can exist as a liquid or solid at room temperature and atmospheric pressure. A "gas" cannot exist as a liquid or solid at normal conditions.

Molecules of each species in the gas phase continually bombard the surface of each particle, giving ample opportunity for chemical reactions, i.e., formation of new molecules, and physical interactions, e.g., transfer of mass between the particle and gas phases. This chapter does not emphasize the most general case in which both chemical reactions and physical interactions occur simultaneously in the atmosphere and during sampling. This is important in particular situations, e.g., when sampling ammonia, acids, and ammonium salts in the ambient atmosphere, and has been discussed elsewhere.(1-4) This chapter emphasizes information needed to make decisions about which phase(s) to sample and techniques for avoiding erroneous sampling results when chemical reactions or condensation/evaporation may occur during sampling. The words "condensation" and "evaporation" are used to indicate the net transport of mass from the gas phase to the particle phase or from the particle phase to the gas phase, respectively.

Air sampling errors being considered include allowing unwanted chemical reactions to occur during sampling, measuring the concentration of a contaminant only in the particle or gas phase when there is a significant fraction in the unsampled phase, and using inappropriate techniques to measure the distribution of a contaminant between the two phases. Avoiding unwanted chemical reactions with reactive gases during sampling is discussed briefly in the next section. This issue has received substantial attention in the literature of environmental air sampling. In the remaining sections, the emphasis is on effects of interphase mass transfer in sampling. The term "semivolatile" is sometimes associated with compounds for which such effects are important. First, the equilibrium distribution of a material between the particle and gas phases will be discussed. Several factors that tend to disturb equilibrium and the time-scale of the approach to equilibrium will then be presented. Finally, techniques for measuring a contaminant's total airborne concentration (concentration in both the particle and gas phases) and approaches to measuring a contaminant's distribution between the two phases will be offered. A draft prestandard has been prepared by a working group of the European Committee on Standardization (CEN) to offer guidance on such issues.(5)

Much of this chapter contains detailed discussions intended to aid the reader who needs a deeper understanding of how particle-gas interactions can influence air sampling. Readers who wish to focus on the practical implications may be most interested in the following: 1) the "Chemical Reactions" section for a brief discussion of how to avoid chemical reactions between collected material and reactive gases; 2) the "General Guidance" subsection of the "Physical Equilibrium" section for rules-of-thumb to guide decisions about whether to sample the particle, gas, or both phases of an aerosol; and 3) the "Sampling Approaches" section for a review of the applicability of different types of sampling instrumentation.

Chemical Reactions

Gases, such as HNO_2, HNO_3, NH_3, NO_2, SO_2, HCl, and HF, in an atmosphere may react with sampled particulate or the filter material used to collect the particulate and lead to erroneous results. This is a more serious problem when sampling times are long as is often the case when sampling outdoors.

A common approach to avoiding these problems is to remove the reactive gas from the air stream with a denuder before the air reaches the filter (see Chapter 19). The sampled air passes through one or more channels in the denuder before reaching the filter. The channel walls are coated with a chemical that will adsorb or react with the unwanted gas and retain it at the wall (Figure 4-1). A properly designed denuder removes the reactive gas from the air stream without removing a significant fraction of the particles being sampled.

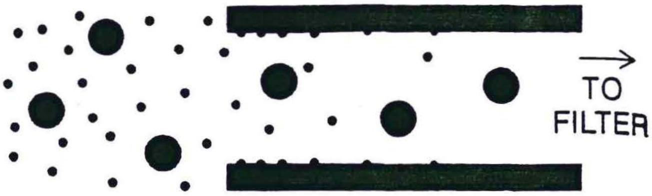

FIGURE 4-1. Schematic diagram of a denuder showing the collection of a reactive gas (small black circles) at the wall by adsorption or chemical reaction. Particles (large gray circles) penetrate the denuder and are transmitted to the filter.

Ideally, a denuder reduces artifacts caused by a gas reacting with collected particles on the filter. However, calculations illustrate the potential for a denuder to introduce artifacts. A denuder section of a sampler collecting particulate from an atmosphere containing HNO_3 and NH_3 gases and NH_4NO_3 particulate in equilibrium with the gases would remove the NH_3, disturb the equilibrium, and tend to cause the chemical species in the particulate to change, possibly leading to an incorrect assessment of the aerosol mass concentration and chemical species.(6, 7) Denuders can be very helpful in avoiding sampling artifacts due to chemical reactions between a reactive gas and collected particles or the filter, but all the possible influences of a denuder should be considered and tested before deciding to include one in a sampling system.(8)

Physical Equilibrium

Gas molecules collide with the surface of suspended particles. At the same time, molecules are ejected from particle surfaces due to thermal energy. At equilibrium, there is no net flux of any species across any solid/gas, liquid/gas, or solid/liquid interface. A solid/liquid interface occurs within particles containing a liquid and undissolved material.

Experimental data relevant to the equilibrium between identical particles and the gas phase can be written in the form:

$$C_{G,i} = f(d_p, C_{P,1}, C_{P,2}, ..) \qquad (1)$$

The symbol C will always imply an airborne mass concentration in this chapter (mass of contaminant per volume of air). The subscript G or P refers to the gas or particle phase, respectively. The mass concentration of the i^{th} contaminant in the gas phase just outside the particle surface $C_{G,i}$ is some function of the composition of the particle surface, which is described here by the mass concentration $C_{P,j}$ of each species in the particle phase of the aerosol. A relation like Equation 1 holds for each species in the gas phase. All the relations are linked because each depends on all constituents in the particle phase. Additional relations exist between the concentration in the liquid phase and the surface composition of solid constituents, if there are any solid/liquid interfaces within particles.

The particle diameter d_p appears in the function because of the Kelvin effect, which increases the equilibrium concentration above a convex surface compared to a planar surface.(9) This factor can be significant for particles that are submicrometer in diameter. For example, a pure submicrometer droplet in an atmosphere which is saturated with the vapor is expected to evaporate completely because it requires a supersaturated atmosphere to reach equilibrium.

When an aerosol consists of particles that differ markedly in composition or size, the equilibrium of each particle class should be considered separately. Each particle size and composition class may influence the composition of the other classes through the gas phase that they share.

In principle, it is possible to predict the distribution of a material between the particle and gas phases if the total airborne mass concentration of each constituent is known and if each of the possible liquid/gas, solid/gas, and solid/liquid interfaces in the system has been sufficiently characterized. Typically, this information is obtained by measuring the concentrations of each constituent on both sides of the interface in a laboratory system. It is often not clear whether available experimental data are relevant because the equilibrium distribution is sensitive to temperature and pressure and may be sensitive to the addition or removal of small quantities of other constituents. Because real atmospheres are often complex and contain many constituents, rigorous prediction of equilibrium conditions is a difficult task. The approach taken here is to present the general form of the relations needed to predict equilibrium and to make some general observations for guidance when making sampling decisions.

Absorption

For aerosols, absorption refers to the dissolution of gas phase materials in droplets. The relation between the gas phase concentration of one of the components adjacent to a droplet surface and the composition of the droplet surface can be expressed in terms of an activity coefficient γ_i(10, 11)

$$C_{G,i} = \gamma_i x_i C^S_{G,i} \qquad (2)$$

where x_i is the mole fraction of the i^{th} material in the droplet surface and $C^S_{G,i}$ is its saturated vapor concentration at the droplet temperature. The superscript S indicates saturation. The saturated vapor concentration is the mass concentration of the vapor above a planar surface of the pure material and can be calculated from the saturated vapor pressure using the Ideal Gas Law. In general, γ is a function of the droplet composition, but it is constrained to assume the value of unity when x_i is unity (pure droplet). The Kelvin effect is not included explicitly in Equation 2, although it should be included for submicrometer particles.(10)

Saturated vapor pressure is a property of the pure material. Caution should be exercised if using saturated vapor pressure data from the literature. The value is temperature sensitive, often changing by an order of magnitude for a 10 to 20°C change in temperature, so application of predictive equations for temperature correction, e.g., the Clausius–Clapeyron equation, may be necessary.(11) In many cases, a literature search may be worthwhile; early measurements of small saturated vapor pressures may be in substantial error and yet may be widely cited. Some saturated vapor pressure information may be available in material safety data sheets, handbooks, and exposure limit documentation.

Equation 2 can be expressed in terms of mass concentrations which are commonly measured when describing an atmosphere

$$C_{G,i} = \gamma_i \frac{M_P}{M_i} \frac{C_{P,i}}{C_P} C^S_{G,i} \qquad \text{droplets} \qquad (3)$$

where a substitution has been made for the mole fraction

$$x_i = \frac{M_P C_{P,i}}{M_i C_P} \qquad (4)$$

The molecular weight of the i^{th} material is M_i and the average molecular weight of the droplet M_P is

$$M_P^{-1} = \frac{M_1^{-1} C_{P,1} + M_2^{-1} C_{P,2} + \ldots}{C_P} \qquad (5)$$

The concentration of all materials in the particle phase C_P is

$$C_P = C_{P,1} + C_{P,2} + \ldots \qquad (6)$$

Equation 3 is very general. It can be used to summarize experimental data on liquid/gas equilibria for most systems across the whole range of possible mole fractions for each component, even when the liquids are not completely miscible.(10, 11)

Specifying the activity coefficient as a function of droplet composition can be quite complex. Simpler and less general relations can successfully characterize liquid/gas equilibria in special cases that commonly occur. Three such special cases will be discussed: ideal liquids, Raoult's Law for solvents, and Henry's Law for dilute solutions.

For ideal liquids, the activity coefficient for each component is unity for all compositions. This is likely to occur for similar liquids, for example, propylene glycol and water.(10,12) The equilibrium of an airborne system of ideal liquids in uniform droplets can be described by

$$C_{G,i} = \frac{M_P}{M_i}\,\frac{C_{P,i}}{C_P}\,C^S_{G,i} \quad \text{ideal liquids} \tag{7}$$

Very few aerosols are likely to consist of ideal liquids.

Raoult's Law has been found to apply to the solvent in many liquid systems even if the solution is not ideal. It can be derived from Equation 2 or 3 by setting the activity coefficient to unity (it should be nearly equal to unity for any material that is nearly pure in the liquid) and applying the resulting equation only to the solvent in a dilute solution(12)

$$C_{G,solv} = \frac{M_P}{M_{solv}}\,\frac{C_{P,solv}}{C_P}\,C^S_{G,solv} \quad \text{solvents} \tag{8}$$

The ratio of the molecular weights and the ratio of the particle phase mass concentrations are both near unity for the solvent in a dilute solution. The Kelvin effect should be included for submicrometer droplets. A common application of Raoult's Law is to describe the relationship between the composition of aqueous droplets and relative humidity RH (in percent) resulting in

$$RH = \frac{C_{G,water}}{C^S_{G,water}}\,100 \tag{9}$$

Henry's Law often applies to a solute in a dilute solution. It states that the partial pressure of the material is proportional to its mole fraction in the solution(12)

$$P_i = x_i H_i \tag{10}$$

The proportionality constant H_i is the Henry's Law coefficient.

Henry's Law is compatible with Equation 2, the general equation for liquids. As the mole fraction of a mate-

a constant γ_i^0.(11) Thus, for a material in a dilute solution, Equation 2 becomes

$$C_{G,i} = \gamma_i^0 x_i C^S_{G,i} \tag{11}$$

Converting the gas phase mass concentration to partial pressure P_i by the Ideal Gas Law

$$P_i = C_{G,i}\,\frac{RT}{M_i} \tag{12}$$

(R is the universal gas constant and T is the absolute temperature) gives for a dilute solution

$$P_i = \gamma_i^0 x_i C^S_{G,i}\,\frac{RT}{M_i} \tag{13}$$

The last result is in the form of Henry's Law. Comparing Equations 10 and 13 shows that the Henry's Law coefficient H_i is related to the activity coefficient for a material in a dilute solution γ_i^0 by

$$H_i = \gamma_i^0 C^S_{G,i}\,\frac{RT}{M_i} = \gamma_i^0 P_i^S \tag{14}$$

The saturated vapor pressure P_i^S has been related to the saturated vapor concentration C^S_{Gi} by the Ideal Gas Law, Equation 12, applied to the saturated state. Solving Equation 14 for γ_i^0 and substituting for γ_i in Equation 3 gives the relation for materials in droplets as dilute solutions in terms of the Henry's Law coefficient

$$C_{G,i} = \frac{H_i}{P_i^S}\,\frac{M_P}{M_i}\,\frac{C_{P,i}}{C_P}\,C^S_{Gi} \quad \text{dilute solutions} \tag{15}$$

The form has been chosen to be similar to that for ideal solutions and solvents.

Many liquid/gas systems, especially those consisting of water and an organic liquid, have been characterized in terms of Henry's Law coefficients either by direct measurement or by extrapolation from measurements in similar systems. All Henry's Law coefficients that have been tabulated have something in common: each is a proportionality constant between the amount in the gas phase and the amount in a dilute (usually aqueous) solution at equilibrium. Unfortunately, different authors define the proportionality constant differently, so Henry's Law coefficients have a variety of units and some Henry's Law coefficients are related to the inverse of another. For example, one list is limited to aqueous solutions and tabulates a Henry's Law coefficient that is related to the inverse of that defined specifying the amount of the material in the dilute aqueous solution are moles per liter and the units of the quantity specifying the amount in the gas phase (partial pressure) are atmospheres, so the Henry's Law coefficient is tabulated with units of moles per liter per atmosphere. The relationship between that Henry's Law coefficient and the one defined in Equation 10 can be derived by relating the concentration of a contaminant in a dilute aqueous solution to its mole fraction. Great care must be taken in applying Henry's Law coefficients obtained from the literature because of the confusing number of definitions and units. The Henry's Law coefficient used in Equations 10, 14, and 15 has units of pressure.

Adsorption

Gas phase materials may adsorb onto the surface of solid particles.(13) Adsorption theories have been discussed in the environmental literature, but there seems to be no definitive compilation of experimental results. One problem has been the difficulty in obtaining valid data on the distribution of an airborne substance between the particle and gas phases due to the artifacts discussed later in this chapter. Some data have been summarized by a relation of the form

$$\log\left(\frac{C_{G,i}C_P}{C_{P,i}}\right) = \frac{m_Y}{T} + b_Y \tag{16}$$

where m_Y and b_Y are constants determined by fitting the data.(14) This relation has been shown to be consistent with the Junge equation which had been proposed earlier.(15) The Junge equation relates the fraction of the material of interest in the particle phase to the saturated vapor pressure of the material at that temperature, P_i^S; the surface concentration of particles, C_S (the total surface area of particles per volume of air); and the Junge constant, c_J, which is determined experimentally,

$$\frac{C_{P,i}}{C_{T,i}} = \frac{c_J C_S}{P_i^S + c_J C_S} \tag{17}$$

where the total airborne concentration of the contaminant $C_{T,i}$ is

$$C_{T,i} = C_{P,i} + C_{G,i} \tag{18}$$

Pankow(15) has derived the theoretical temperature dependence of the Junge constant assuming linear Langmuir adsorption and has shown that the resulting equation describing equilibrium conditions is equivalent to Equation 16. Solving Equations 17 and 18 for $C_{G,i}$ results in the equilibrium relation

$$C_{G,i} = \frac{P_i^S C_{P,i}}{c_J C_S} \tag{19}$$

For materials with a melting point higher than the temperature of the atmosphere being sampled, it has often been found preferable to use the saturated vapor pressure of the liquid extrapolated down to the atmospheric temperature (called the subcooled liquid saturated vapor pressure) rather than the saturated vapor pressure above the pure crystalline solid.(16) Application of the Ideal Gas Law and straightforward algebraic manipulation lead to a form similar to Equations 3, 7, 8, and 15 for the equilibrium relation for adsorption

$$C_{G,i} = \frac{RT}{M_i c_J \sigma_p} \frac{C_{P,i}}{C_P} C_{G,i}^S \quad \text{adsorption} \tag{20}$$

where the specific surface area (area per mass) of the particle phase σ_P is

$$\sigma_p = \frac{C_S}{C_P} \tag{21}$$

Sorption

The association of gas phase material with particles by either absorption or adsorption is called sorption. It has been suggested that it may be adequate to describe the gas phase mass concentration of an air contaminant in equilibrium with either solid or liquid particles by a fairly simple relation:(17)

$$C_{G,i} = B_i \frac{C_{P,i}}{C_P} C_{G,i}^S \tag{22}$$

$C_{P,i}$ is the mass concentration of the i^{th} contaminant in the particle phase. C_P is the mass concentration of all materials in the particle phase. $C^S_{G,i}$ is the saturated vapor concentration of the i^{th} material or the extrapolated saturated vapor concentration for the subcooled liquid, if the melting point of the pure material is above the temperature of the atmosphere. The Kelvin correction may be needed for submicrometer particles. The proportionality "constant" B_i is temperature dependent and also depends on the materials involved. One utility of this approximation is that although B_i depends on a variety of characteristics of the particles and contaminant gases, it may be slowly varying. For example, it may be nearly constant for similar solid/gas and liquid/gas systems.(17)

Equation 22 emphasizes that the distribution of a material between the particle and gas phases depends strongly on its saturated vapor concentration and the amount of particulate available. One advantage of this equation for summarizing air sampling data on the distribution of a particular contaminant of interest between the particle and gas phases is that it asserts a relationship between the equilibrium concentration of the contaminant in the gas phase and the particle phase mass concentrations that might be measured in a field study, as well as the contaminant's saturated vapor concentration. Generally, B_i and its variability (including its temperature dependence) will be determined experimentally for the particular situation.

Formulating the particle/gas distribution relationship in terms of a new proportionality constant B_i does not mean that all the previous data on such systems must be discarded. Available data on adsorption of material onto solid particles and absorption into droplets can be converted to information about B_i. Comparing Equation 22 with Equations 3, 7, 8, 15, and 20 shows that the form of each is similar and gives relationships which can be expected to hold between the proportionality constant B_i in Equation 22 and other experimental quantities that are sometimes tabulated for solid/gas and liquid/gas systems

$$B = \gamma_i \frac{M_P}{M_i} \quad \text{droplets} \tag{23}$$

$$B = \frac{M_P}{M_i} \quad \text{ideal liquids} \tag{24}$$

$$B = \frac{M_P}{M_{solv}} \quad \text{solvents} \tag{25}$$

$$B = \frac{H_i}{P_i^S} \frac{M_P}{M_i} \quad \text{dilute solutions} \tag{26}$$

$$B = \frac{RT}{M_i c_J \sigma_p} \quad \text{adsorption} \tag{27}$$

Additional field studies will be needed to indicate whether the relatively simple form of Equation 22 is adequate to describe particle-gas equilibria in real systems. However, it seems to have a solid theoretical basis for both adsorption and absorption and is related to previously tabulated quantities, as shown in Equations 23–27.(17) The form of Equation 22 suggests quantities that may be important to measure when dealing with the distribution of materials between the particle and gas phases and indicates a relationship which should be tried when attempting to summarize experimental data.

In the special case of the sorption of semi-volatile organic compounds on atmospheric particles, observations suggest that an even better description of the equilibrium conditions than Equation 22 is

$$C_{G,i} = \text{fn}(K_{OA})\, C_{P,i} \tag{28}$$

where K_{OA} is the octanol-air partition coefficient for the compound and fn is some function determined from experimental data.(18-20) The utility of this relation is that the function appears to be the same for all semi-volatile organic compounds in several classes. There is no experimental evidence that this relation will apply to most workplace aerosols, although it is plausible that it would apply in workplaces having a substantial organic component in the airborne particles.

Single Component System

Consider the case of a single component aerosol. This occurs when the airborne particles consist of only one constituent because none of the other constituents of the gas phase dissolve into or adsorb onto the particles. Calculation of the distribution of the contaminant between the gas and particle phases at equilibrium is straightforward. If the total airborne concentration, i.e., the concentration in the particle phase plus that in the gas phase, is larger than the saturated vapor concentration, the difference between the two is the mass concentration in the particle phase. The saturated vapor concentration is the concentration in the gas phase. Otherwise, if the total airborne mass concentration is less than the saturated vapor concentration, any particles evaporate completely and all the contaminant is in the gas phase. For small particles, the gas phase concentration that is in equilibrium with the pure droplet may be significantly higher than the concentration over a planar surface (the saturated vapor concentration), so a Kelvin effect correction may be needed.

Multiple Component System

In most cases, particles are not pure and two or more materials must be considered. For example, water vapor is ubiquitous on Earth and dissolves into or adsorbs onto most particles to some extent. Some general discussions of the equilibrium of simplified or actual airborne systems have been presented in the literature of environmental and occupational air sampling.(21–26) Calculation of the Kelvin effect is more complicated for a two-component droplet than for a single component.(27) The correction for the equilibrium vapor concentration above a curved surface is often small for droplet diameters larger than a micrometer and will not be explicitly included here.

Ignoring the Kelvin effect and assuming identical particles, there are four unknowns in describing the equilibrium of a two-component system: a particle phase and a gas phase mass concentration for each of the components. If the total mass concentrations of both components are specified and the two interdependent relations between the mass concentrations of the two components in the gas phase and the composition of the particles similar to Equations 1 or 22 are known, then the four equations can be solved for the four unknowns.(21) In principle, the equilibrium of a system consisting of more than two components can be predicted using analogous information for each component.

General Guidance

Consideration of two-component systems emphasizes the importance of four basic facts that also hold for more complex systems:

A. The mass concentration of a contaminant in the gas phase is less than or equal to its saturated vapor concentration at that temperature.
B. If the particle phase has significant excess capacity to adsorb or dissolve the contaminant, the mass concentration of the contaminant in the gas phase is significantly less than its saturated vapor concentration.
C. The mass concentration of a contaminant in the particle phase is the difference between the mass concentration in the gas phase and its total mass concentration in the atmosphere.
D. The mass concentration of each contaminant in the particle phase is less than or equal to the total mass concentration of all airborne particles.

Applying these somewhat elementary facts leads to three useful generalizations (rules-of-thumb):

1. Sample only the particle phase when the saturated vapor concentration of a substance C^S_{Gi} is much less than its total airborne mass concentration $C_{T,i}$

$$C^S_{G,i} << C_{T,i} \tag{29}$$

2. Sample only the gas phase when the total mass concentration of all constituents in the particle phase C_P is much smaller than the total airborne mass concentration of a contaminant $C_{T,i}$

$$C_p << C_{T,i} \tag{30}$$

3. Sample both the particle and gas phases when neither of the above two conditions is met.

When the saturated vapor concentration of a substance is of the same order as or is larger than its total airborne mass concentration, much of the mass might be expected to be in the gas phase. However, if the material occurs as a dilute solution in the particle phase or is strongly bound to particle components, a significant fraction of the mass may be in the particle phase. For example, both observations and calculations suggest that some pesticides and other organic compounds can have a significant fraction of the total airborne material in the particle phase at high humidities.(21,22,28)

The three rules-of-thumb can be applied once some information is known about the system under consideration. The most helpful pieces of information are the identities of the major constituents and their saturated vapor concentrations and some estimate of their total airborne mass concentrations. These ideas are consistent with previous publications that emphasized considering the ratio of the saturated vapor concentration to the exposure limit for the material under consideration when deciding whether to sample the particle, gas, or both phases of an atmosphere.(21, 22) This ratio has also been called the "vapor/hazard ratio number."(29)

Substances for which the American Conference of Governmental Industrial Hygienists (ACGIH®) had established Threshold Limit Values (TLVs®) were reviewed to provide examples of materials for which too little might be known to judge whether the particle, gas, or both phases should be sampled as well as examples of substances for which the available information might seem to suggest erroneously that only one phase should be sampled.(22)

Table 4-1 illustrates the results from applying the rules-of-thumb to a number of assumed atmospheres when deciding whether to sample the particle, gas, or both phases. Each atmosphere contains a contaminant with a known saturated vapor concentration of 0.001, 0.01, 1, or 100 mg/m^3. For an assumed molecular weight of 100, the Ideal Gas Law gives the corresponding saturated vapor pressures: 3×10^{-6}, 3×10^{-4}, 3×10^{-2}, and 3 Pa (2×10^{-8}, 2×10^{-6}, 2×10^{-4}, and 2×10^{-2} mm Hg). The mass concentration of all airborne particles, C_P, is assumed to be either 0.05 mg/m^3, which may be typical of the general outdoor environment and many workplaces, or 5 mg/m^3, which may be typical of dusty workplaces or light fog. Table 4-1 illustrates the large range of conditions for which both the particle and gas phases should be sampled. Whenever it is not clear that only one phase should be sampled, both phases should be sampled.

The discussion in this section applies if an airborne system is in or near equilibrium. Sometimes a system is not near equilibrium. The following two sections consider

TABLE 4-1. Examples of Sampling Decisions in a Range of Assumed Atmospheres

Mass concentration of all airborne particulate, C_p (mg/m^3)	Total airborne mass concentration of contaminant, $C_{T,i}$ (mg/m^3)	Saturated vapor concentration of contaminant at 25°C, $C^{\xi}_{G,i}$ (mg/m3)			
		0.0001	0.01	1	100
0.05	0.0001	PG	PG	PG	PG
0.05	0.01	P	PG	PG	PG
0.05	1	*	*	G	G
0.05	100	*	*	*	G
5	0.0001	PG	PG	PG	PG
5	0.01	P	PG	PG	PG
5	1	P	P	PG	PG
5	100	*	*	*	G

P = Sample particulate phase only, because $C^{\xi}_{G,i} << C_{T,i}$

G = Sample gas phase only, because $C_p << C_{T,i}$

PG = Sample both phases because neither condition is met.

* = Unphysical, because no atmosphere can meet both conditions.

conditions that disturb the equilibrium of a system and the time a system needs to reach equilibrium.

Disturbance of Equilibrium

Some kinds of changes will disturb the equilibrium of an airborne system and require mass to be transferred between the phases to attain a new equilibrium consistent with the new conditions. For example, an atmosphere may not be in equilibrium immediately after a source injects a gaseous or particulate contaminant into it or just after it is pulled into a sampler. Detailed calculations of the system dynamics can be performed using similar experimental information to that needed to predict equilibrium (equilibrium concentrations across interfaces), plus information about transport through a phase, e.g., the diffusion of gas molecules through air. The equations are complicated by the transport of latent heat which occurs during condensation and evaporation. The formulation and results of detailed computational models are beyond the scope of this discussion.

Atmospheric Changes

Conditions that may disturb an airborne system's equilibrium include a change in temperature or atmospheric pressure, addition or removal of contaminant mass, or addition of clean air (dilution).(30) The direction in which each of these changes tends to move the equilibrium will be discussed briefly.

An increase in temperature tends to increase the fraction of a substance in the gas phase due to higher thermal energy promoting the ejection of molecules from surfaces. A decrease in temperature tends to decrease the fraction in the gas phase.

A decrease in atmospheric pressure with no change in temperature, for example, due to the slow expansion of a volume, decreases the gas phase concentration at a particle surface and tends to lead to evaporation of material from the particle. The decrease in the mass concentration of the particle phase due to the expansion does not influence the new equilibrium, because equilibrium depends most fundamentally on gas phase concentrations and particle phase composition, not particle phase concentration. Increases in atmospheric pressure have an opposite effect.

Sources or sinks of vapor disturb the equilibrium and may lead to significant condensation onto or evaporation from particles. For example, an increase in humidity is likely to lead to increased water in the particle phase. The loss of particles, for example, by sedimentation, or the addition of particles which have the same composition as the particles that are already equilibriated with the atmosphere does not disturb the equilibrium of the system. However, the addition of particles of a different composition will disturb the equilibrium in general.

Dilution with clean air decreases the vapor concentration at the particle surface and tends to promote evaporation of volatile contaminants from the particles.

Sampling

The process of sampling an atmosphere has the potential to disturb the particle-gas equilibrium in the sampled air. This can lead to biased sampling results. Characteristics of four types of sampling instruments, filter samplers, cascade impactors, denuders, and electronic monitors, will be discussed briefly. Some effects of inhaling an aerosol will also be mentioned.

After a filter sampler collects particles (see Chapter 13), they remain on the filter surface and are exposed to the air that is sampled subsequently. Even if there are no chemical changes due to reactive gases, physical changes in the particles can occur. During extended sampling, the atmosphere is likely to change in temperature or in the concentration of gas phase species, including water vapor. Such changes will require volatile components to evaporate from or absorb/adsorb onto the particles collected on the filter, possibly leading to substantial decreases or increases in the overall mass or the mass of volatile components.(31) For example, ammonium nitrate evaporates from filters, if the air sampled subsequently is relatively clean.(32, 33) Much less evaporation into clean air occurs from ammonium nitrate collected in an impactor (see Chapter 14) than in a filter, apparently because of the relatively thick boundary layer of air and the decreased surface area of the collected material.(34) Another situation that can occur with extended sampling times is clogging of the filter with particulate. The decreased pressure experienced by some of the collected particulate may lead to evaporation of some materials.

Another type of error can occur in filter sampling. Some filter materials adsorb some vapors from the air stream.(35–38) This contributes to an increase in mass and may allow the materials to be extracted from the filter for chemical analysis. Such errors lead to an overestimate of the mass of material in the particle phase. This problem can be reduced by choosing a filter material that is not prone to adsorbing the types of vapors which are in the atmosphere to be sampled. Filter adsorption can be detected in the field by placing a second filter downstream of the first and checking for an increase in mass, assuming the first filter is not such an efficient adsorber that all the vapor is scrubbed from the air stream. Adsorption on the back-up filter may not parallel that on the front filter, so correction of the mass increase on the front filter by that on the back-up filter may not be accurate.(35) Inefficient particle collection by the first filter would confound detection of vapor adsorption by this method, because it would also lead to an increase of mass of the second filter.

In a cascade impactor (see Chapter 14), the sampled air is drawn through a nozzle to accelerate the particles, so the larger ones will impact on a collection surface and be separated from the smaller particles and the air stream. Then the process is repeated with smaller nozzles that achieve higher air velocities and allow smaller particles to be collected on other surfaces. During its passage through each nozzle, the air experiences a pressure drop. The decrease in pressure tends to promote evaporation of volatile components from particles.(39) In smaller nozzles and higher speed jets, the air may be cooled somewhat. This tends to promote condensation of volatile materials onto particles.(40) Because the two effects act in opposite directions, predicting the net effect of passage through a cascade impactor depends on the details of the situation, but the potential for significant particle-gas interactions should not be overlooked.

If a sampler incorporates a denuder as the first stage to remove reactive gases (see Chapter 19), any particle components that are in equilibrium with that gas will tend to adjust to the removal of the gas from the sampled air stream.(6) Some have suggested that measuring the distribution of a material between the particle and gas phases of an atmosphere could be accomplished using a denuder to collect material from the gas phase followed by a filter to collect particulate. One difficulty with this approach is that there will be a tendency for the particles to evaporate in the denuder. This situation will be considered in more detail later in this chapter.

Electronic sampling instruments, e.g., real-time monitors, may have high speed inlets and contain pumps, motors, and lights that generate heat. Drawing air into warm instruments will promote evaporation of volatile components from particles; decreasing the pressure will also promote evaporation; and cooling in the jet will promote condensation.(40–43)

Inhaling air typically warms and humidifies it. Warming the air tends to cause volatile materials to evaporate from particles. High humidity tends to cause water-soluble particles to absorb water vapor. This typically dilutes other constituents in the particles and causes other volatile components to be absorbed also.(10) However, more complex interactions can occur. For example, water might drive off less polar compounds adsorbed on some materials. If the particles consist entirely of substances that are immiscible with water, high humidity may have little effect. It is difficult to generalize about the effects of inhaling an atmosphere on the distribution of material between the gas and particle phases. It is clear that the distribution of a material between the particle and gas phases that is measured in the atmosphere may not be the same distribution that occurs in the respiratory tract.

Time-scale of Evaporation and Condensation

When considering the effects of evaporation and condensation on sampling results, it is often useful to know the time-scale, an estimate of the time required for a significant fraction of the evaporation or condensation to occur as the system approaches its new equilibrium. This can be helpful in judging whether a recently generated system, e.g., one consisting of droplets that were ejected into relatively clean air, has had sufficient time to approach equilibrium. One approach for estimating the time-scale for evaporation of a contaminant from the particle phase is to divide the decrease in contaminant mass in the particle phase by the initial evaporation rate.(10) The resulting time-scale for evaporation τ_e is

$$\tau_e = \frac{C^0_{P,i} - C^f_{P,i}}{C_P} \frac{\rho_p d_p^2}{12 D_i C^S_{G,i} \left(B_i \frac{C^0_{P,i}}{C_P} - S_i \right)} \quad \textbf{(31)}$$

The initial and final mass concentrations of the contaminant in the particle phase are $C^o_{P,i}$ and $C^f_{P,i}$, respectively. The particle density is ρ_p and the diffusion coefficient of the vapor in air is D_i. The saturation S_i is the gas phase concentration of the contaminant (far from a particle surface) divided by the saturated vapor concentration. It has been assumed that the mass concentration of vapor at the particle surface can be described successfully by Equation 22. Equation 31 neglects the slower evaporation that occurs due to the latent heat of the evaporating material cooling the particles as well as the Kelvin effect and the correction for gas transport from small particles.(10)

Substituting plausible values for the density (1 g/cm^3) and the diffusion coefficient (0.1 cm^2/s) and applying the equation to the special case of complete evaporation of the contaminant ($C^f_{P,i} = 0$) into air that is substantially depleted of vapor (S_i negligible) results in the order-of-magnitude estimate:

$$\tau_e \approx 8\,\text{sec} \frac{\left(\frac{d_p}{1 \mu m} \right)^2}{\left(\frac{B_i\, C^S_{G,i}}{1\,\text{mg/m}^3} \right)} \quad \textbf{(32)}$$

If the value of B_i is unknown, a first estimate of the time-scale of evaporation can be obtained by assuming B_i is unity. For pure droplets ($B_i = 1$) near room temperature, the time-scale for evaporation of a 1-µm water droplet $C^S_{G,i}$ = 17,000 mg/m^3) into dry air is about a half millisecond; that of a 10-µm glycerol droplet ($C^S_{G,i}$ = 0.5 mg/m^3) is about 27 min. Equation 32 also provides a reasonable estimate for the time-scale of growth by condensation for a particle that contains no contaminant initially and grows into one with diameter d_p.(10)

Sampling Approaches

There has been little discussion of the issue in the literature, but it could be argued that in most health-related air sampling, the quantity that is the most important to measure accurately is the total airborne mass concentration without regard to whether the material is in the gas or particle phase. Volatile materials may move between the gas and particle phases because of a change in conditions, including after inhalation, but the total airborne mass concentration is unchanged.(10) This makes it a practical first choice for measurement.

In some cases, it may be desirable to measure the distribution of a compound between the two phases instead of only the total airborne mass concentration. For example, there may be compounds for which the toxic effects are thought to differ significantly depending on whether the material existed in the particle or gas phase just prior to inhalation.(44) Also, the choice of control technology may depend on which phase dominates. Both sampling the total airborne concentration and sampling the distribution between the two phases are discussed in the following sections.

Total Airborne Concentration

Measuring the total airborne concentration requires an efficient particle collector and an efficient vapor collector. Two approaches have been found suitable. One is to place the vapor collector, such as a tube containing an efficient sorbent, downstream of an efficient particle collector, such as a filter.(44–51) One problem with the reverse configuration, placing the vapor collector upstream of the particle collector, is that material might evaporate from the particles which are collected on the filter and be lost. The second approach that has been used successfully is to apply a coating of a material to the filter that either adsorbs or reacts chemically with the air contaminant being sampled.(52, 53) A variation of this approach is to preload the filter with a particulate sorbent.(54) If done properly, the approach of using a coated or preloaded filter results in a compact and convenient sampler with all the collected material on one substrate for analysis.

Other approaches might provide satisfactory results, but care must be taken to ensure that the collection efficiency is sufficiently high for both phases in each sampling situation. Impingers are versatile in allowing the liquid to be changed to match the compound being collected, but the collection efficiency for submicrometer particles is low.(55) Impingers collect solid isocyanates more effectively than coated filters, since the required derivatization occurs more quickly.(56)

The particle collection efficiency of some sorbent beds may be sufficient to allow measurements of the total airborne concentration of some compounds.(49,57,58) These devices should not be used without experimental validation of their suitability for the specific application.

Techniques for measuring the total airborne concentration have been much less widely discussed in the literature of workplace air sampling than in the literature of air sampling in the general environment. However, such techniques have been proposed for organophosphorus pesticides, fluoride, formaldehyde, and isocyanates.(5, 59–64)

Particle/Gas Distribution

In cases where high precision is not required and some experimental phase distribution data are available to validate a relation like Equation 22, it would be possible to estimate the distribution between the particle and gas phases after measuring only the total airborne concentration of the contaminant and the concentration of all airborne particulate. In order to use a relation like Equation 22, it would be necessary to assume that the atmosphere is near equilibrium, i.e., sufficient time has passed since the atmosphere's equilibrium was last disturbed, as discussed in the previous section. In most cases, reliable information about the distribution of a material between the particle and gas phases of an atmosphere can only be obtained by measurements in that or similar atmospheres.

There does not appear to be any universally accepted method for measuring the mass concentrations of an air contaminant in the particle and gas phases separately. Many approaches have been described in the literature, but questions arise about the accuracy of the results. Three approaches are presented here that seem suitable for a range of sampling conditions, but each has characteristics that might lead to erroneous results in some sampling situations. Because of the ease with which the particle/gas equilibrium is disturbed and mass is transferred between the two phases, measurement of the distribution of an air contaminant between the particle and gas phases is much more difficult than measurement of the total airborne mass concentration.

A sampling system consisting of an efficient particle collector followed by an efficient vapor collector was one of the two configurations recommended for measuring the total airborne mass concentration of a contaminant. It has also been used in attempts to measure the distribution of a contaminant between the gas and particle phases. The vapor collector must be removed from the particle collector at the end of the sampling period and stored separately to avoid evaporation of the volatile contaminant from the particles and transport to the vapor collector.

The most common configuration, called a "filter pack," consists of a filter as the particle collector and a sorbent as the vapor collector. The particle phase concentration is calculated from the mass collected on the filter and the gas phase concentration from that collected in the sorbent (Figure 4-2).(16, 65) A filter pack might be suitable for measuring the average concentration in each phase over the sampling period if two conditions are met: 1) the filter does not adsorb the vapor and 2) the chemical composition and physical characteristics of the sampled atmosphere are constant during the entire sampling period.(66) If the filter adsorbs vapor, the particle phase mass concentration will be overestimated and the gas phase underestimated.(35–38, 67) As mentioned previously, adsorption onto a filter might be detected by placing a second filter downstream of the first, but correcting for such adsorption is problematic.(35, 68) If the sampled atmosphere does not stay constant, mass collected from the particle phase onto the filter will tend to evaporate and be transferred into the vapor collector whenever the mass concentration of the contaminant in the gas phase decreases. Also, mass in the gas phase of the air being sampled will be transferred to collected particles on the filter whenever the mass concentration in the gas phase increases. As a result, filter packs may not be valid for health-related sampling from the occupational or general environment, although they may be valid for sampling from a controlled atmosphere, e.g., inhalation exposure chambers or a process line.

Replacing the filter by a cascade impactor appears to reduce the interaction between particles that have deposited on the collection surfaces and the air drawn

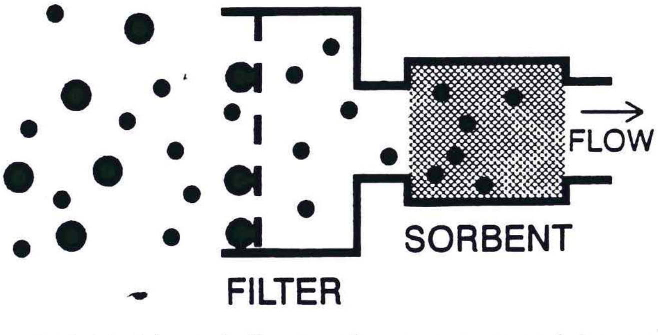

FIGURE 4-2. Schematic diagram of a common approach to measuring the distribution of a contaminant between the particle and gas phases of an atmosphere. Particles (large gray circles) with associated molecules of a contaminant in the gas phase (small black circles) are collected on the filter. Vapor penetrating the filter is collected in the sorbent. Particle and gas phase concentrations are calculated from the masses collected on the filter and in the sorbent, respectively. Potential errors include vapor adsorption by the filter material and transfer of contaminants between the gas phase and particles already collected on the filter if the atmosphere changes temperature, humidity, or composition.

through the device subsequently, reducing the severity of some of the artifacts.(69) The problem remains that the air which enters the vapor collector has passed over all the previously collected particles and significant mass transfer between the gas and collected particles may have occurred.

Replacing the filter by a virtual impactor reduces this problem, because the larger particles are not collected on a surface over which air subsequently passes on the way to the vapor collector.(70-72)

A second approach uses a denuder to remove vapor from the sampled air stream (see Chapter 19), followed by an efficient collector of both particles and vapor (Figure 4-3). The particle and vapor collector may be a treated filter or a filter followed by an adsorbent. The gas phase concentration is calculated from the mass collected in the denuder and the particle phase concentration from that collected in the particle and vapor collector.(73–79)

If the material collected in the denuder cannot be removed quantitatively for analysis, the "denuder difference method" may be used.(80) Two samplers are operated in parallel. One is a particle and vapor collector and the other consists of a denuder to collect the material from the gas phase followed by a particle and vapor collector. The difference between the masses of material collected in the two particle and vapor collectors is taken to be the mass in the gas phase.

In another variation, the vapor may be transported preferentially into a parallel air stream because it has a higher diffusion coefficient than the particles.(81)

These denuder-related approaches might be expected to give valid results if: 1) there is insignificant particle deposition in the denuder;(82, 83) 2) the denuder collects all or a known fraction of the contaminant mass which was in the gas phase when the air entered the sampler without breakthrough;(84) and 3) there is insignificant particle evaporation and subsequent transfer of that contaminant mass to the denuder walls. Item 2 is easier to attain using denuders with narrow channels because the small distance between the bulk of the sampled air and the coated walls allows efficient collection of vapor at higher flow rates. The third item is the most troublesome and may be impossible to attain for some materials. During the time the particles reside in an atmosphere that has been depleted of vapor, some material will evaporate from the particles. In order to have this mass transfer be negligible, the amount that evaporates must be a negligible fraction of the amount in the particle phase and must be a negligible fraction of the amount that was in the gas phase before the aerosol entered the denuder.

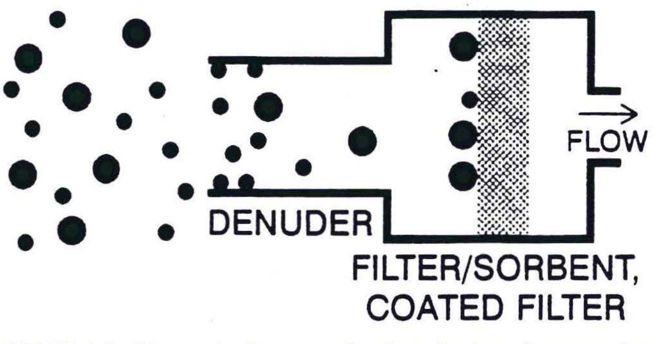

FIGURE 4-3. Schematic diagram of a denuder-based approach to measuring the distribution of a contaminant between the particle and gas phases of an atmosphere. Vapor molecules (small black circles) are collected at the wall of the denuder. Particles (large gray circles) with associated volatile contaminants are collected by a filter that is either treated or followed by a suitable sorbent to trap vapor molecules. Potential errors include particle deposition in the denuder and significant evaporation of the particles while surrounded by vapor-depleted air.

Consideration of a simple case, particles with a single volatile component and the vapor in equilibrium with them, is instructive. The sampled air's residence time in the denuder τ_r can be estimated as the denuder's volume divided by the sampling flow rate. The characteristic time for complete evaporation/desorption into vapor-depleted air is given in Equation 32. Only a negligibly small fraction of the volatile component's mass in the particles will evaporate during the transit time if

$$\tau_r << \tau_e = 8\,\text{sec}\frac{\left(\dfrac{d_p}{1\mu m}\right)^2}{\left(\dfrac{B_i\, C^S_{G.i}}{1\,\text{mg/m}^3}\right)} \qquad (33)$$

Another condition is necessary to ensure that the mass of contaminant that does evaporate from the particles is negligibly small compared to the mass of material which was initially in the gas phase. Otherwise, the mass of contaminant collected at the denuder walls will be in error. Recalling that the characteristic time of evaporation is defined here as the volatile contaminant's mass in the particle phase divided by the initial evaporation rate, an order of magnitude estimate of the mass of material that evaporates from the particles per volume of air can be written as the particle mass divided by the characteristic time of evaporation times the residence time. A relationship sufficient to ensure that the amount of evaporated contaminant is negligibly small compared to the amount originally in the gas phase, expressed in terms of saturation, is:

$$\frac{C_{P.i}}{\tau_e}\tau_r << S_i C^S_{G.i} \qquad (34)$$

Substituting for τ_e using Equation 32 and substituting $C_{G,i}$ using Equation 22 for $S_i\ C^S_{G,\ i}$ under the assumption that the particles were in equilibrium with the vapor before entering the denuder gives:

$$\tau_r << 8\,\mathrm{sec}\frac{\left(\dfrac{d_p}{1\mu\mathrm{m}}\right)^2}{\left(\dfrac{C_p}{1\ \mathrm{mg/m}^3}\right)} \qquad (35)$$

The residence time cannot be made arbitrarily small because all or a known fraction of the vapor molecules must have time to diffuse to the wall of the denuder and be collected (see Chapter 19). Evaporation of particles in a denuder will lead to negligible errors if both the contaminant's saturated vapor concentration and the concentration of all materials in the particle phase are sufficiently small according to Equations 33 and 35, given the assumptions stated in their derivation. Negligible evaporation of particles in a denuder is more likely for outdoor environmental sampling than for sampling in dusty/misty workplaces where C_P is likely to be higher. These generalizations should hold even for atmospheres containing several volatile and nonvolatile components.

A third approach to measuring the distribution of a contaminant between the gas and particle phases has been described.(85–87) The approach is to measure the total concentration in both phases by methods outlined already and place a suitable passive sampler nearby to measure the vapor concentration (Figure 4-4). The concentration in the particle phase would be estimated by subtraction. If only a small fraction of the total airborne contaminant were in the particle phase, this estimate might be quite imprecise because it is determined by subtracting two measurements. Another source of significant error might be the deposition of particles on the front surface of the diffusive sampler. If such particles were allowed to remain in that position sufficiently long and the surrounding vapor concentration fluctuated, material in the particles might evaporate during periods of lower vapor concentration and erroneously contribute a significant amount to the mass collected on the sorbent of the diffusion sampler. This would lead to an overestimate of the fraction of contaminant in the gas phase.

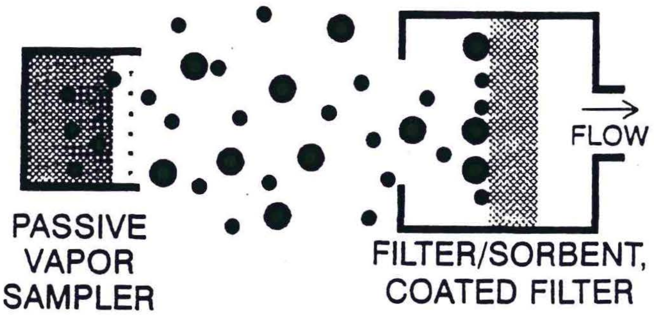

FIGURE 4-4. Schematic diagram of an approach to measuring the distribution of a contaminant between the particle and gas phases of an atmosphere. Vapor molecules (small black circles) and particles (large gray circles) are collected in an active sampler containing a treated filter or filter followed by a sorbent to measure the total airborne concentration of the contaminant. Vapor only is collected in the passive sampler. The particle concentration is estimated by subtraction. Potential errors include deposition of particles on the passive sampler and high uncertainty in estimating the particle concentration when it is much smaller than the vapor concentration.

Summary and Conclusions

Particle and gas phase interactions can lead to errors in air sampling results. Some errors include allowing unwanted chemical reactions to occur during sampling, measuring the concentration of a contaminant only in the particle or gas phase when there is a significant fraction in the unsampled phase, and using inappropriate techniques to measure the distribution of a contaminant between the two phases.

Errors due to chemical reactions between a reactive gas and particles that have been collected on a filter can be reduced by passing the air through a suitable denuder before it reaches the filter.

It is important to understand the distribution of an air contaminant between the particle and gas phases and the potential for changes in that distribution during sampling. Three pieces of information are helpful in judging whether it is necessary to sample the gas, particle, or both phases of an atmosphere: the saturated vapor concentration of the contaminant, a rough estimate of the total airborne concentration of the contaminant in the atmosphere being sampled, and a rough estimate of the concentration and composition of the particles in the atmosphere. The distribution of a contaminant between the particle and gas phases depends on temperature, pressure, particle composition, and the gas phase concentration of the contaminant. The processes of sampling or inhalation may change the distribution between the phases significantly.

It is arguably more important to measure the total airborne concentration of a contaminant, i.e., the concentration in the particle phase plus that in the gas phase, than to measure the distribution between the phases. The total airborne concentration can be measured by a sampler consisting of an efficient filter followed by an efficient sorbent or can be measured by a filter that is treated with a material which adsorbs or reacts with the vapor.

When it is necessary to measure the distribution of a contaminant between the particle and gas phases, no universally acceptable technique appears to be available. The common approach of placing a sorbent downstream of a filter is prone to errors if the filter adsorbs vapor or if the atmosphere's composition changes. Replacing the filter with a virtual impactor reduces many of these errors. The approach of placing a denuder capable of collecting the vapor upstream of a collector of the particles and vapor that penetrate the denuder is prone to errors if the denuder is not optimized for the application. In some cases, it may be difficult to avoid significant errors due to evaporation of the contaminant from the particles while they reside in vapor–depleted air in the denuder. A third approach to measuring the distribution of a contaminant between the gas and particle phases is available. The total airborne concentration is measured by an active sampler and the vapor concentration is measured by a passive sampler. This approach has not been widely used, yet. Other approaches are likely to be suggested in the future, but measuring the distribution will always be much more difficult than measuring the total airborne concentration.

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