APTI 435: ATMOSPHERIC SAMPLING COURSE, 5TH EDITION

Student Manual

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The preparation of this manual was overseen by the Environmental Protection Agency (EPA), and the revision of materials was coordinated and managed by the Tidewater Operations Center of C^2 Technologies, Inc., Newport News, Virginia.

This course revision has been updated through extensive editing as well the incorporation of new information. Acknowledgement and thanks are extended to the subject matter advisors who participated in this effort: Stephen Szulecki, M.S., former Director of Rutgers Air Pollution Training Program at Rutgers University, NJ; Francesco Maimone, M.S., former Co-Director of Rutgers Air Pollution Training Program at Rutgers University, NJ; and Dennis Mikel, Physical Scientist at EPA's Air Quality Assessment Division, Research Triangle Park, NC.

ENVIRONMENTAL PROTECTION AGENCY

APTI 435: Atmospheric Sampling Course

Student Manual

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Chapter 4: Particulate Matter Sampling 4-1

G.1 Working with Numbers

Chapter 2

This chapter will take approximately 1.25 hours to complete.

Basic Gas Properties and Mathematical Manipulations

OBJECTIVES

Terminal Learning Objective

At the end of this chapter, the student will be able to identify basic gas properties and mathematical manipulations.

Enabling Learning Objectives

2.1 Differentiate between temperature scales and absolute temperature.

2.2 Identify the types of pressure and the instruments used.

2.3 Identify the ideal gas laws.

2.4 Describe gas density.

2.5 Define the term *Reynolds Number*.

2.6 Explain equations used to identify basic gas properties.

2.7 Identify units of measurements that measure air pollution parameters.

2.8 Describe use of references and definitions.

2.1 Temperature

The Fahrenheit and Celsius Scales

The range of units on the Fahrenheit scale between the freezing and boiling point of water at one atmosphere (atm) pressure is 180 (212°F-32°F= 180°F); on the Celsius scale, the range is 100 (100°C-0°C = 100°C). Therefore, each Celsius degree is equal to 9/5 or 1.8 Fahrenheit degrees. To convert from one system to the other, the following equations can be used:

(Eq. 2-1)
$$°\text{F} = 1.8°\text{C} + 32$$

(Eq. 2-2)
$$°\text{C} = \frac{(°\text{F} - 32)}{1.8}$$

Where: *°F = degrees Fahrenheit*
°C = degrees Celsius

Absolute Temperature

Experiments in which a gas volume is determined as a function of temperature (at a constant pressure) yield results similar to the data presented in Figure 2.1(a). The solid portion of each line represents the gaseous state. If each line is extrapolated (dashed portion of line) to a volume of zero, they all intersect at a common temperature (-273.15°C or -459.67°F). This is the temperature at which a gas, if it did not condense, would theoretically have a volume of zero. This temperature (-273.15°C or -459.67 °F) is called *absolute zero.* Another temperature scale, developed by and named after English physicist Lord Kelvin in 1848, begins at absolute zero and has temperature intervals equal to Celsius units. This absolute temperature scale is in units of *Kelvin* (K). It is not proper to use the term or symbol for "degrees" in association with the *Kelvin scale.* A similar scale was developed, in 1859, by William Rankine, a Scottish engineer and physicist, to parallel the Fahrenheit scale and is called the *Rankine scale* (°R). The following formulas can be used to convert temperatures to their respective absolute scales.

(Eq. 2-3) $$K = {}^{\circ}C + 273.16$$

(Eq. 2-4) $$^{\circ}R = {}^{\circ}F + 459.67$$

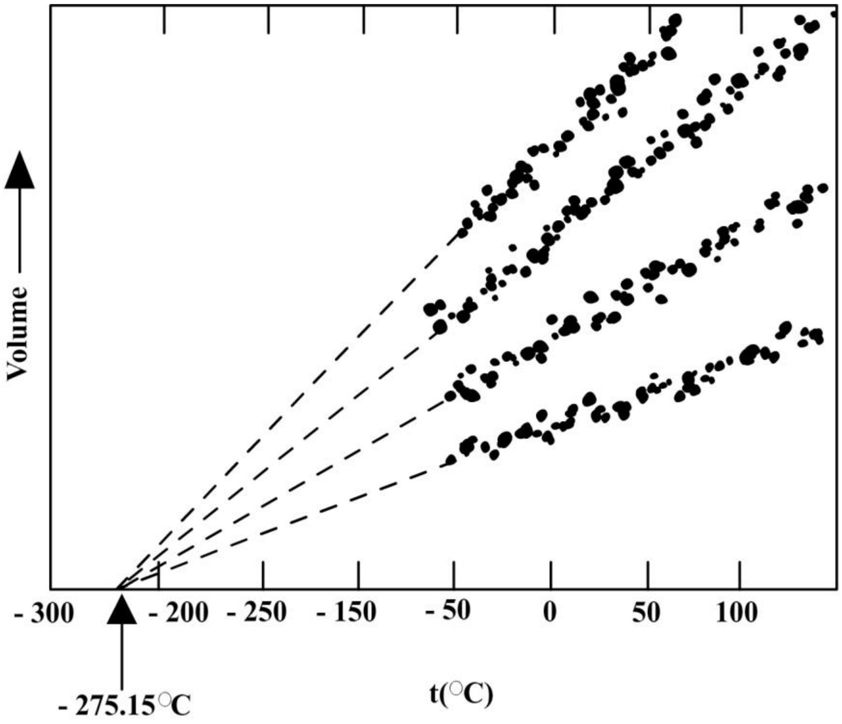


Figure 2-1(a). Temperature relationships.

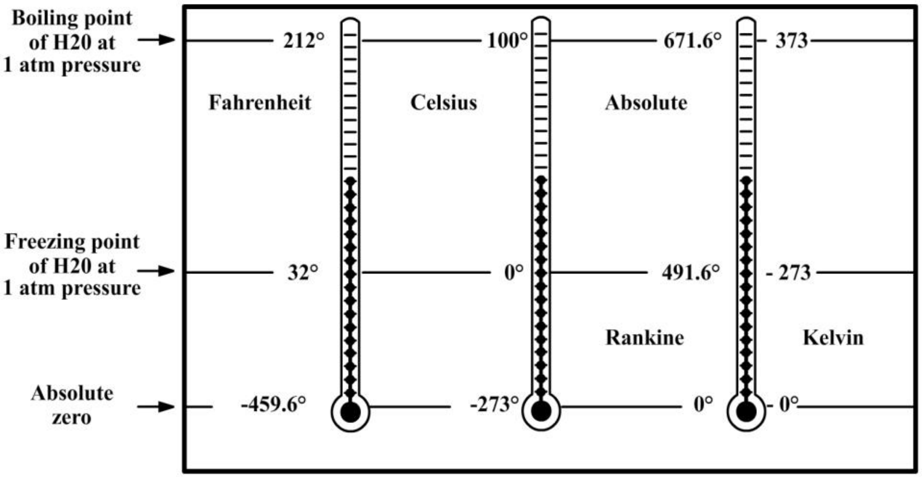


Figure 2-1(b). Relationships of the absolute temperature systems.

Relationships of the absolute temperature systems are shown graphically in Figure 2-1(b). The symbol "T" will be used throughout this manual to denote absolute temperatures, and the "t" will be used to indicate Fahrenheit or Celsius degrees. The absolute temperatures are always in volume calculations involving temperature and pressure.

2.2 Pressure

Definition of Pressure

A body may be subject to three kinds of stress: shear, compression, and tension. Fluids are unable to withstand tensile stress; hence, they are subject to shear and compression only. Unit compressive stress in a fluid is termed *pressure* and is expressed as *force per unit area.*

Pressure

Metric	English
gm_f/cm^2	lb_f/in^2 (psi)

Pressure is equal in all directions at a point within a volume of fluid and acts perpendicular to a surface.

Barometric Pressure

Barometric pressure and atmospheric pressure are synonymous. These pressures are measured with a barometer and are usually expressed as inches or millimeters of mercury. Standard barometric pressure is the average atmospheric pressure at sea level, 45° north latitude, at 35°F, and is equivalent to a pressure of 14.696 pounds-force per square inch exerted at the base of a column of mercury 29.921

inches high (in the English System). In the metric system, standard barometric pressure is equivalent to a pressure of 1033.23 grams-force per square centimeter exerted at the base of a column of mercury 760 mm high. Weather and altitude are responsible for barometric pressure variations.

Torricelli Barometer

The Torricelli, or mercurial, barometer was first used by one of Galileo's students, Evangelista Torricelli, in 1643. A mercurial barometer is made by sealing a tube, about 32 inches long, at one end. The tube is filled with mercury. It is then inverted and placed into a container that is partially filled with mercury. The mercury in the tube will fall until the weight of the mercury in the tube is equal to the force of the air pressure on the mercury in the container. As shown in Figure 2-2, the manometer and the mercurial barometer work on the same principle – atmospheric pressure being measured with reference to a vacuum.

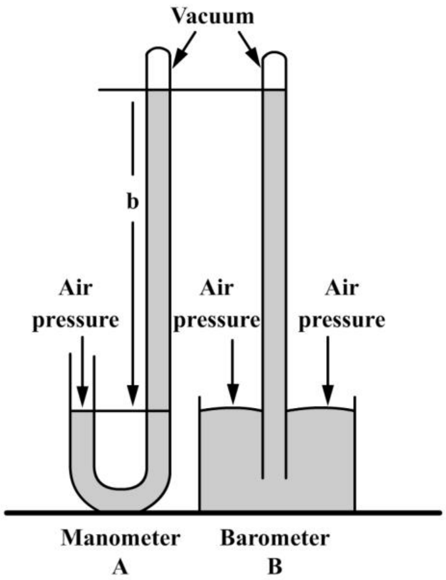


Figure 2-2. The manometer and mercurial barometer.

Fortin Barometer

Since the mercurial barometer is the most accurate measurement (calibration uncertainty of 0.001 to 0.03% of reading) of atmospheric pressure, it is still in wide use today. The most common modified version of the mercurial barometer is the Fortin type shown in Figure 2-3.

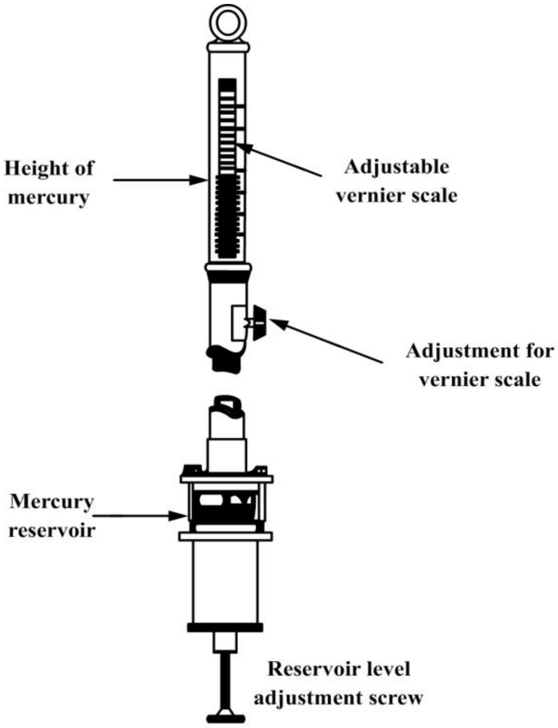


Figure 2-3. Fortin barometer.

The height of the mercury column in a Fortin barometer is measured from the tip of the ivory index point (see the enlargement in Figure 2-4) to the top of the mercury column. The mercury level in the glass cylinder (ambient-vented cistern) is adjusted until the ivory index point just pricks the surface of the mercury. This is done by turning the datum-adjusting screw. Then the vernier scale is adjusted until the bottom of it is even with the top of the mercury meniscus. After the vernier scale is adjusted, the height of the mercury column is read.

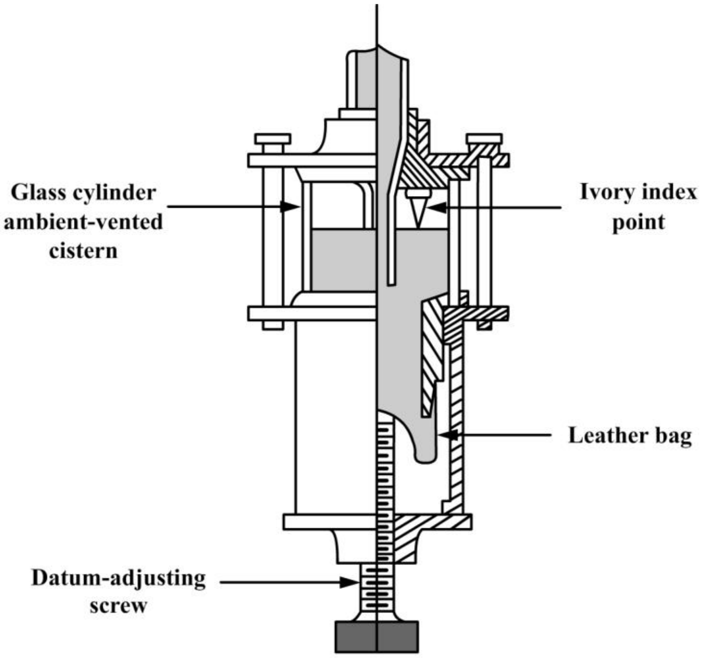


Figure 2-4. Blow-up of Fortin barometer.

A typical vernier scale is shown in Figure 2-5. The barometric pressure indicated in the figure is determined in the following way: the bottom of the vernier scale indicates not only the integer component of the barometric pressure, but also the tenths components – in this case, 29.9. The hundredths component is indicated by the match between the outer scale and the vernier – in this case, 0.04. The readings are totaled to determine the barometric pressure: 29.9 + 0.04= 29.94 in. Hg. The equivalent metric reading is 76.05 cm.

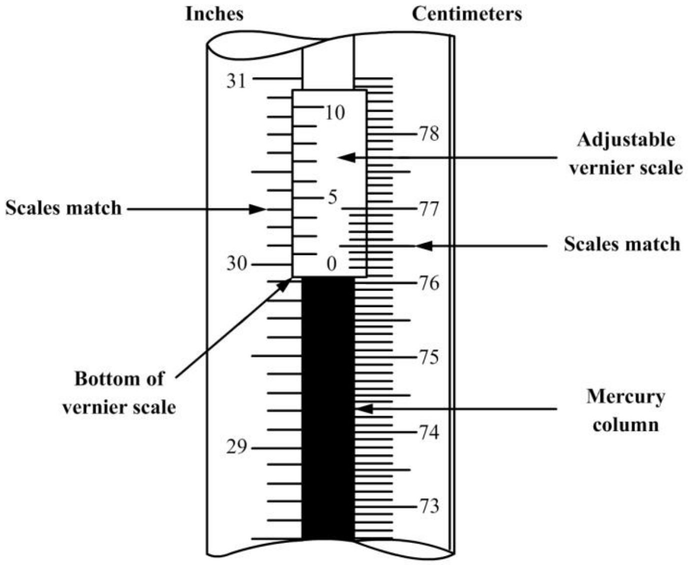


Figure 2-5. Blow-up of vernier scale.

Aneroid Barometer

The aneroid barometer is usually not as accurate as a Torricelli barometer. However, aneroid barometers are more widely used because they are smaller, more portable, less expensive, and easier to adapt to recording instrumentation than are Torricelli barometers.

The aneroid barometer usually consists of a metal chamber, bellows, or sylphon (accordion-like) cell that is partially evacuated. A spring is used to keep the metal chamber from collapsing (see Figure 2-6). The width of the chamber is determined by the balance between the spring and the force exerted by the atmosphere. The width of the chamber is indicated by a pointer and scale that can be calibrated to read directly in units of pressure (i.e., millimeters or inches of mercury, etc.). The pointer movement can be amplified by using levers. Read-out systems can vary from visual scales to recording devices. The combination of an aneroid barometer and an automatic recording device is called a barograph.

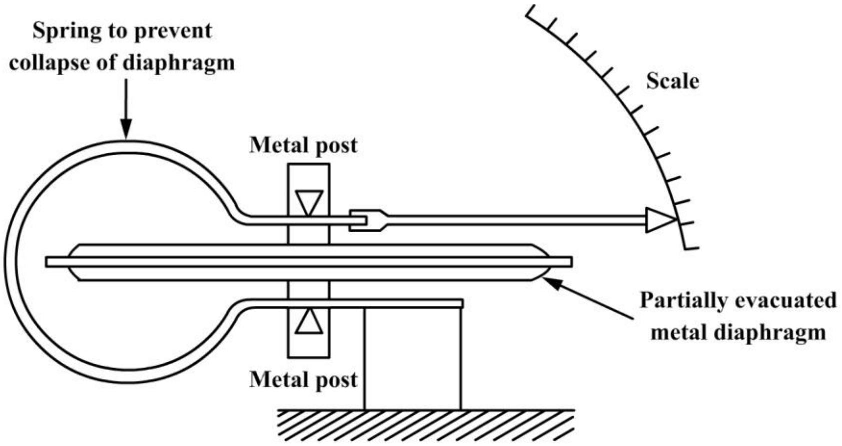


Figure 2-6. Aneroid barometer.

Pressure Transducers

A transducer is a device that is activated by power from one system and supplies power in some other form to a second system. Conventional pressure transducers use an elastic element that converts the energy from a pressure differential into a displacement of a mechanical device. An example of a mechanical pressure transducer is shown in Figure 2-7. Other pressure transducers convert the mechanical displacement into an electrical signal. An example of an electrical transducer is shown in Figure 2-8. Electrical pressure transducers have become very popular because the signal is easy to measure, control, amplify, transmit, and record.

Other variations on the pressure transducer include the use of the principles of conductivity and capacitance to measure pressure. A *strain gauge* uses the change in conductivity which results from the deflection of a material as it senses pressure changes. The deflection of the sensing material alters its resistance which is related to the change in pressure. Another technology uses the change of capacitance due to change of the distance between charged plates to calculate the pressure.

Pressure sensors can vary drastically in technology, design, performance, application, suitability, and cost. A conservative estimate is that there are 50 different technologies and hundreds of companies making pressure sensors.

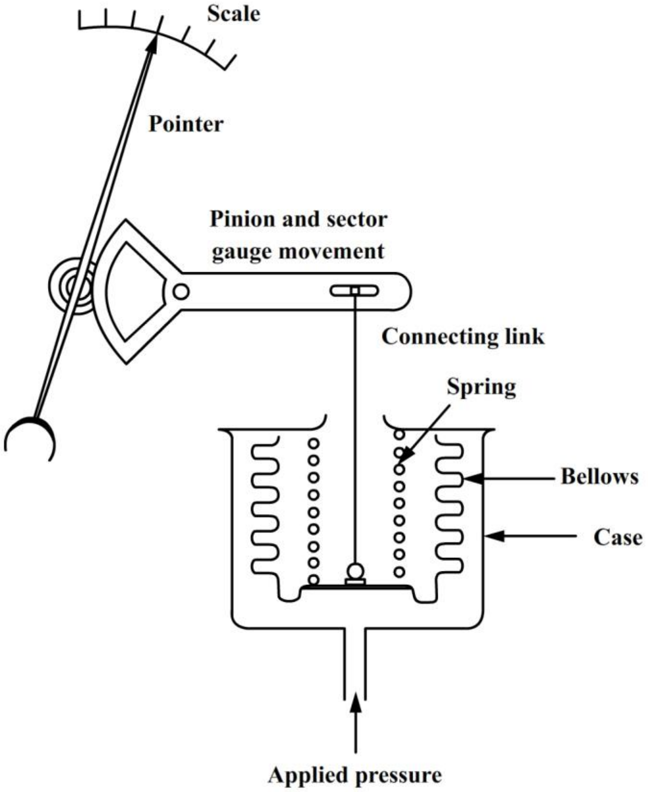


Figure 2-7. Mechanical pressure transducer.

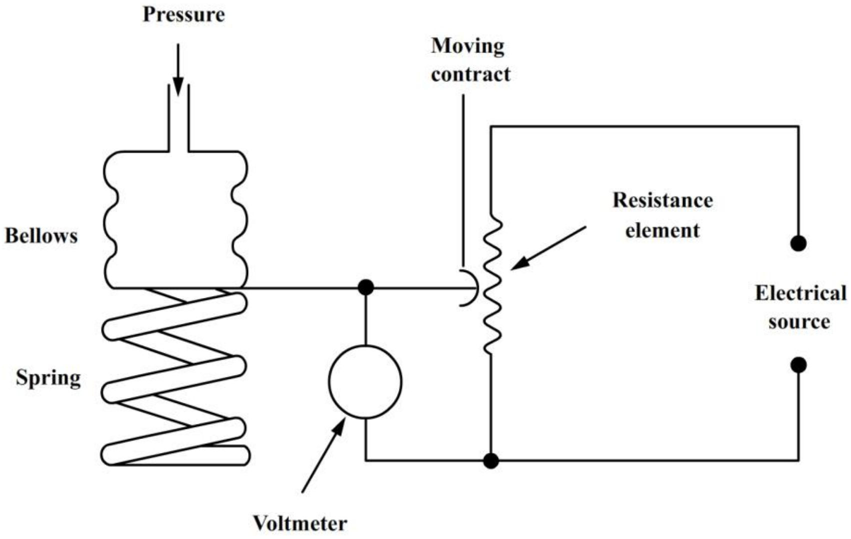


Figure 2-8. Electrical pressure transducer.

Gauge Pressure

Gauges indicate the pressure of a system relative to ambient barometric pressure. If the pressure of the system is greater than the pressure prevailing in the atmosphere (atmospheric pressure), the gauge pressure is expressed as a positive value; if smaller, the gauge pressure is expressed as a negative. The term "vacuum" designates a negative gauge pressure. The abbreviation "g" is used to specify a gauge pressure. For example, *psig* means pounds-force per square inch gauge pressure.

The pressure you measure when determining if your car tire is properly inflated is a gauge pressure. In fact, the term "inflated" refers to a system which is pressurized, and as such we know it represents a positive pressure relative to atmospheric pressure. The opposite is true for an evacuated SUMMA flask used to collect an air sample. In this case, the air is drawn out of the flask prior to sampling, creating a negative gauge pressure relative to atmospheric pressure, referred to as a *vacuum*. At the time of sampling, the valve of the flask is opened, and the pressure differential between the atmosphere and the flask (negative relative to the atmosphere) creates the driving force necessary to draw in the sample.

Absolute Pressure

Because gauge pressure (which may be either positive or negative) is the pressure relative to the prevailing atmospheric pressure, the gauge pressure, added algebraically to the prevailing atmospheric pressure (which is always positive), provides a value that is called "absolute pressure." The mathematical expression is:

(Eq. 2-5)

$$P = P_b + p_g$$

Where:

P = *absolute pressure*

P_b = *atmospheric pressure*

p_g = *gauge pressure*

Note: P, P_b, and p_g must be in the same units of pressure before they can be added (i.e. all must be in inches of mercury, mm of mercury, etc.).

The abbreviation "a" is sometimes used to indicate that the pressure is absolute. For example, *psia* means pounds per square inch absolute pressure. Conventionally, a gauge pressure is denoted with a lower-case "p" and a pressure on an absolute basis with an upper-case "P."

Equation 2-3 allows conversion of one pressure system to the other. The relationship of the two pressure systems is shown graphically in Figure 2-9 using two typical gauge readings, 1 and 2. Gauge reading 1 is above the prevailing atmospheric pressure and, therefore, is expressed as a positive value. Gauge reading 2 is below the prevailing atmospheric pressure and is expressed as a negative value. Gauge reading 3 has both sides open to the atmosphere; hence, the gauge pressure is zero.

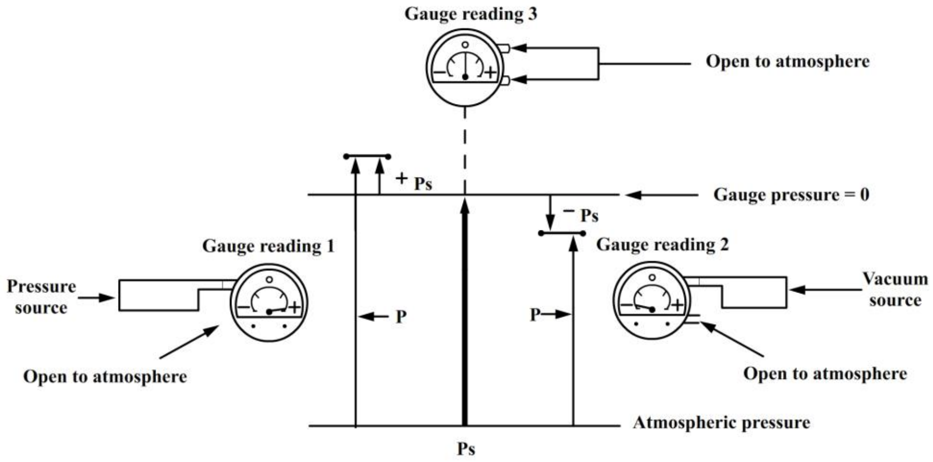


Figure 2-9. Absolute-atmospheric-gauge pressure relationship.

Example Problems

Problem 1:
The primary pressure gauge of a regulator attached to a compressed nitrogen cylinder indicates a reading of 2000 psig. An aneroid barometer mounted on the wall indicates that the atmospheric pressure is 14.2 psi. What is the absolute pressure inside the tank?

Solution:

$$P = P_b + p_g = 14.2 + 2000$$
$$P = 2014.2 \text{ psia}$$

Problem 2:
A water manometer is used to measure the pressure inside an evacuated flask. The water manometer indicates that the evacuated flask has a vacuum of 26 inches of water. A nearby Fortin barometer indicates that atmospheric pressure is 752.6 mm Hg. What is the absolute pressure inside the flask?

Solution:
Before p_g and P_b can be added to give *P,* both must be in the same unit of pressure. It is most common for p_s to be converted to the same units as P_b since P_b is in much larger units.

Since 1 inch of Hg = 13 inches H_2O (Hg is 13 times denser than water):

$$(26\,\text{inches H}_2\text{O})\left(\frac{1\,\text{inch Hg}}{13\,\text{inches H}_2\text{O}}\right)\left(\frac{25.4\,\text{mm}}{1\,\text{inch}}\right) = 50.8\,\text{mm Hg}$$

Now p_g and P_b can be added. p_g is negative because the evacuated flask is at a vacuum, or below atmospheric pressure.

$$P = P_b + \rho_g = 752.6\text{mm Hg} + (-50.8\text{mm Hg})$$
$$P = 701.8\text{mm Hg}$$

The Concept of Pressure-Head

Pressure-head is the height of a column of fluid required to produce a given pressure at its base.

The relationship between pressure and pressure-head is:

(Eq. 2-6)
$$p = \varrho_f h\left(\frac{g}{g_c}\right)$$

Where:
p = *pressure, force/area*
ϱ_f = *density of fluid, mass/volume*
g = *local acceleration due to gravity, length/time*^{2}
g_c = *dimensional constant*
h = *pressure-head in terms of* ϱ_f *length*

Pressure-head may be expressed in terms of any fluid that is convenient, e.g., Hg or H_2O.

Dalton's Law of Partial Pressure

When gases or vapors (having no chemical interaction) are present as a mixture in a given space, the pressure exerted by a component of the gas-mixture at a given temperature is the same as would be exerted if the gas-mixture filled the whole space alone. *The pressure exerted by one component of a gas-mixture is called its partial pressure. The total pressure of the gas-mixture is the sum of the partial pressures.* Expressed mathematically:

$$p_{total} = \sum p_i$$

Where:
p_{total} = *total pressure exerted by the system*
p_i = *pressure of each component of the system*
$\sum p_i = p_1 + p_2 + \ldots + p_{19}$
($\sum$ = *sum of*)

2.3 The Ideal Gas Laws

Ideal gases are gases whose molecules do not attract one another and which occupy no part of the whole volume. Although there are no gases which have these properties, real gases, which deviate very slightly from ideal gas behavior under ordinary temperature and pressure conditions, may be considered to be ideal gases.

Boyle's Law

Boyle's Law states: when the *temperature (T)* is held constant, the *volume (V)* of a given mass of an ideal gas of a given composition varies inversely as the absolute pressure (*P*), i.e.:

$$V \alpha \frac{1}{P} \quad \text{(at constant } T\text{)}$$

$$(\alpha = \text{proportional to})$$

One can see that, as the pressure on a gas system increases, the volume of the gas system will decrease and vice versa.

Charles' Law

Charles' Law states: when the *pressure (P)* is held constant, the *volume (V)* of a given mass of an ideal gas of a given composition varies directly as the *absolute temperature (T), i.e.,*:

$$V \alpha T \quad \text{(at constant } P\text{)}$$

In other words, as the temperature of a gas system increases, the volume will also increase and vice versa.

The Law for Ideal Gases

Both Boyle's and Charles' Laws are satisfied in the following equation:

(Eq. 2-7) $$PV = nRT$$

Where:
P = *absolute pressure*
V = *volume of a gas*
T = *absolute temperature*
R = *universal gas-constant*
n = *number of moles of a gas*

A *mole* of a substance is the substance's molecular weight, expressed in mass units, where the substance's molecular weight is the sum of the atomic weights of the atoms which compose the substance.

We know that

$$n = \frac{m}{M}$$

Where: m = *mass of a gas*
M = *molecular weight of a gas*

therefore: $$PV = nRT = \frac{m}{M}RT$$

The units of *R* depend upon the units of measurement used in the equation. Some useful values are:

$$(1)\ \ \mathrm{R} = 0.082\,(L)\,(atm)\,(K)^{-1}(g\text{-}mole)^{-1}$$
$$(2)\ \ \mathrm{R} = 62.4\,(L)\,(mm\ Hg)\,(K)^{-1}(g\text{-}mole)^{-1}$$

Where the units are: $V(L)$
$m(g)$
$M(g/g\text{-}mole)$
$T(K)$
P *[atm for (1) or mm Hg for (2)]*

Different values of *R* can be obtained by utilizing the appropriate conversion factors.

Molar Volume ($\overline{V}$)

One mole of any gas at 273 K (0° C) and 760 mm Hg will occupy 22.414 liters. This constant is obtained from the ideal gas law. From Equation 2-5:

If: P = *760 mm Hg*
n = *1 mole*
R = $62.4\,(L)(mmHg)\,(g\text{-}mole)^{-1}(K)^{-1}$
T = *273 K*
V = $\overline{V}$ *(molar volume)*

then:

$$P \times V = n \times \mathrm{R} \times T$$
$$(760\ mm\ Hg)\,(V) = (1\ g\text{-}mole)\left(62.4\,\frac{L \cdot mm\ Hg}{g\text{-}mole\ K}\right)(273\ K)$$
$$V = \frac{(1)(62.4)(273)}{760}\,\ell$$
$$V = 22.414L = \overline{V}$$

Therefore, one mole of an ideal gas at 273 K and 760 mm Hg occupies

22.414 liters (L). In other words, the molar volume ($\overline{V}$) of an ideal gas at 273 K and 760 mm Hg is 22.414 L/mole.

At EPA standard conditions (760 mm Hg, 298 K), one mole of any gas will occupy 24.46 L. The volume per mole constant for any gas at a given pressure and temperature is called the *molar volume* and is symbolized by $\overline{V}$.

2.4 Gas Density

Finally, we can use the ideal gas law to estimate gas density. Density is the ratio of the mass of a material to the volume that material occupies. For accurate values, gas densities should be determined from reference texts. However, an estimate of the gas density can be determined from the ideal gas law. Recognizing that the number of moles is given by mass (m) divided by molecular weight (MW), the ideal gas law may be written:

(Eq. 2-8)

$$PV = nRT = \frac{m}{M}RT$$

$$\frac{m}{V} = \varrho = \frac{PM}{RT}$$

Where:

ϱ = *density*
P = *absolute pressure*
M = *molecular weight*
T = *absolute temperature*
R = *universal gas constant*

Another method of determining density is by utilizing the fact that there are 24.46 liters per g-mole at 298 K and 760 mm Hg.

In the relationship $\varrho = m/V$, if V is in terms of molar volume, V(L/ g-mole of a gas at STP), then m must be in terms of molecular weight, $M(\mathrm{g/g\text{-}mole})$. So $\varrho = m/V$ at a given temperature and pressure.

$$\varrho = \frac{M\frac{298}{T}\frac{P}{760}}{24.46}$$ *, corrected to standard temperature and pressure conditions*

Where:

ϱ = *gas density (g/L)*
M = *molecular weight (g/g-mole)*
24.46 = *molar volume (L/g-mole)*
298 = *temperature (K) at standard conditions*
T = *temperature (K) at actual conditions*
760 = *pressure (mm Hg) at standard conditions*

P = *pressure (mm Hg) at actual conditions*

Standard Conditions for Atmospheric Sampling

To be able to compare gas sampling data collected by various agencies and other organizations, all gas volumes must be corrected to a set of predetermined ("standard") conditions. For atmospheric or ambient sampling, these conditions are:

25°C or 298 K, and 760 mm Hg.

The equation used to correct volumes sampled to standard conditions is:

(Eq. 2-9)

$$V_2 = (V_1)\left(\frac{P_1}{P_2}\right)\left(\frac{T_2}{T_1}\right)$$

$$V_2 = (V_1)\left(\frac{P_1}{760\ mm\ Hg}\right)\left(\frac{298\ K}{T_1}\right)$$

$$V_2 = (V_1)(0.39)\left(\frac{P_1}{T_1}\right)$$

Where:

V_2 = *volume of gas at 2nd conditions or at P_2 and T_2, L*

V_1 = *volume of gas at 1st conditions of P_1 and T_1, L*

T_1 = *initial temperature of gas, K*

T_2 = *final temperature of gas--in this case, 298 K*

P_1 = *initial pressure of gas, mm Hg*

P_2 = *final pressure of gas--in this case, 760 mm Hg*

$0.39 = \frac{298}{760}$

The term "standard conditions for temperature and pressure" is abbreviated STP.

Origin and Definition of Viscosity

Viscosity is the result of two phenomena: (a) intermolecular cohesive forces and (b) momentum transfer between flowing strata caused by molecular agitation perpendicular to the direction of motion. Between adjacent strata of a flowing fluid a shearing stress results that is directly proportional to the velocity gradient (Figure 2-10). *Viscosity is often defined as resistance to flow.*

The relationship of these forces is shown in Equation 2-8.

(Eq. 2-10)

$$g_c T = \mu \frac{dv}{dy}$$

Where:

g_c = *dimensional constant*

T = *unit shearing stress between adjacent layers of fluid*

$\frac{dv}{dy}$ = *velocity gradient*

μ = *proportionality constant (viscosity)*

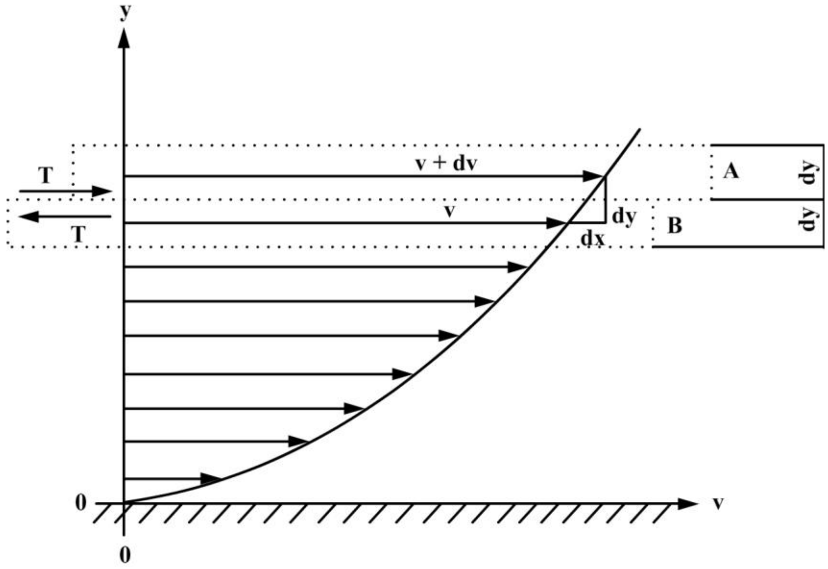


Figure 2-10. Velocity gradient.

The proportionality constant, μ, is called the coefficient of viscosity, or merely *viscosity*. It should be noted that the pressure does not appear in Equation 2-10, indicating that the shear (T) and the viscosity (μ) are independent of pressure. (Viscosity actually increases very slightly with pressure, but this variation is negligible in most engineering problems.)

Kinematic Viscosity

Kinematic viscosity is defined according to the following relationship:

(Eq. 2-11)

$$v = \frac{\mu}{\varrho}$$

Where:

v = *kinematic viscosity*

μ = *viscosity of the gas*

ϱ = *density of the gas (note the absence of dimensions of force)*

Liquid Viscosity versus Gas Viscosity

Liquid Viscosity

In a liquid, transfer of momentum between strata having different velocities is small, compared to the cohesive forces between the molecules. Hence, shear stress (T) is predominantly the result of intermolecular cohesion. Because forces of cohesion decrease with an increase in temperature, the shear stress decreases with an increase in temperature. Equation 2-10 shows that shear stress is directly proportional to the viscosity. Therefore, liquid viscosity decreases when the temperature increases.

Gas Viscosity

In a gas, the molecules are too far apart for intermolecular cohesion to be effective. Thus, shear stress is predominantly the result of an exchange of momentum between flowing strata caused by molecular activity. Because molecular activity increases with temperature increases, the shear stress increases with a rise in the temperature. Therefore, gas viscosity increases when the temperature increases.

Determination of Viscosity of Gases

The viscosity of a gas may be found accurately from the following formula:

(Eq. 2-12)

$$\frac{\mu}{\mu^\circ} = \left(\frac{T}{273.1}\right)^{n}$$

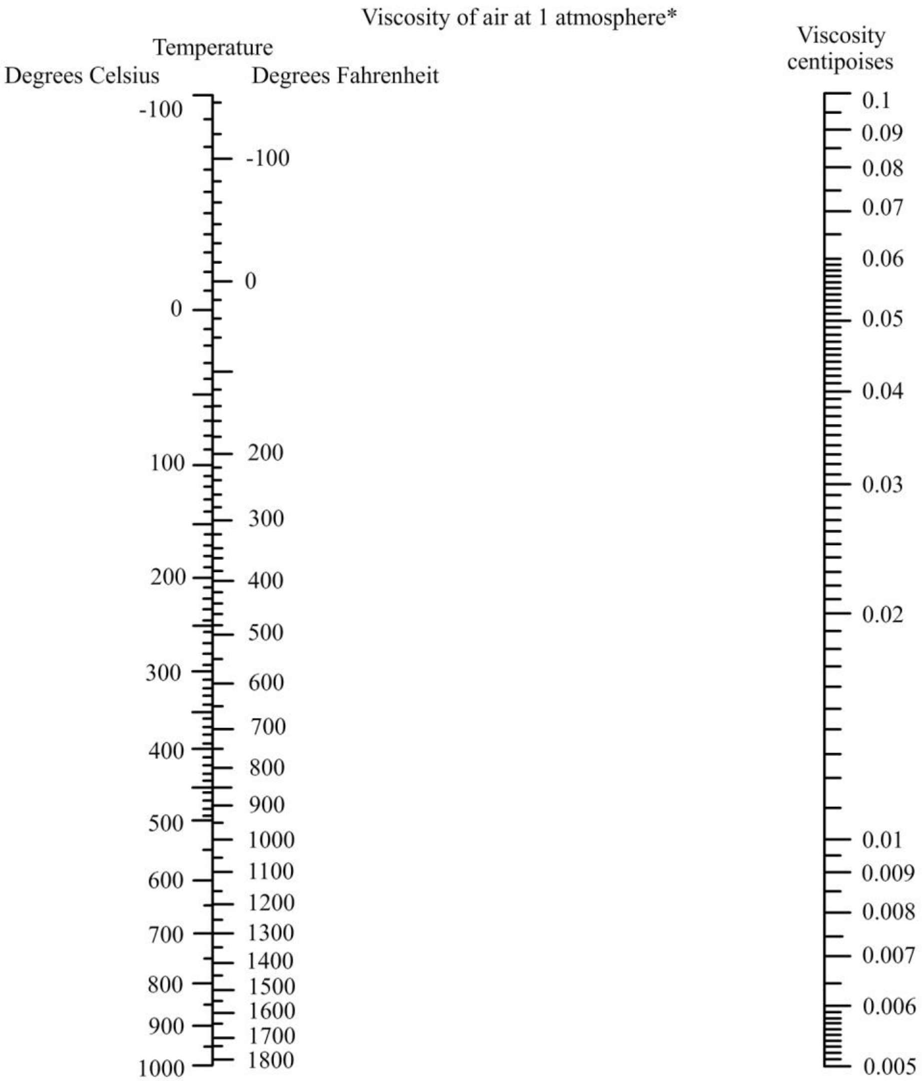
Where: μ = *viscosity at temperature T (K)*

μ° = *viscosity at 0°C and prevailing pressure*

T = *absolute prevailing temperature (K)*

n = *an empirical exponent ($n = 0.768$ for air)*

The viscosity of air and other gases at various temperatures and at a pressure of 1 atmosphere can be determined from the nomograph in Figures 2-11 and 2-12, or from Equation 2-10. The unit of the viscosity coefficient is the poise:
1 poise = gm/cm•sec. A centipoise (cp) is equal to 10^{-2} poise.



(1)centipoise	$(10)^{-2}\,\frac{gm}{cm - sec}$ $(10)^{-2}$ poise	$209(10)^{-6}$ $\frac{lb_f - sec}{ft^2}$	$2.09(10)^{-6}$ $\frac{alug}{ft - sec}$	$6.72(10)^{-4}$ $\frac{lb_m}{ft - sec}$

*Perry, J.H. Chemical engineer's Handbook. McGraw-Hill Book Co., New York (1950)

Figure 2-11. Viscosity nomograph for air.

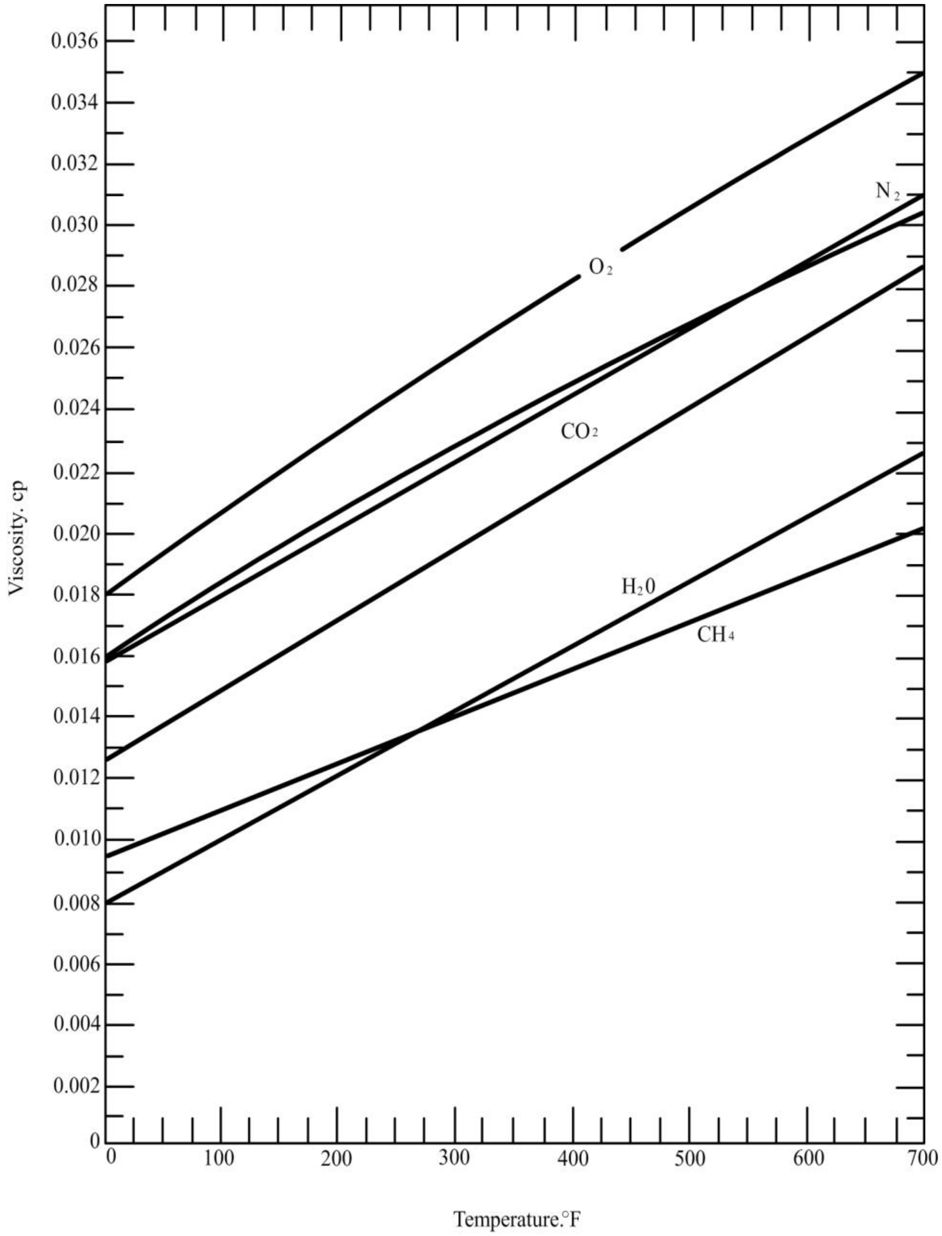


Figure 2-12. Viscosity nomograph of various gases at 1 atmosphere.

2.5 Reynolds Number

In 1883, Osborne Reynolds experimented with laminar and turbulent flow. His basic experiment was to inject a dye in a small section of fluid flowing in a tube and find where the flow changed from laminar to turbulent flow. He found that the flow could change abruptly and it could be predicted based on the ratio of inertial forces to viscous forces in a flowing fluid. A typical inertial force per unit volume of fluid is $\rho v^2/L$. A typical viscous force per unit volume of fluid is $\mu v/L^2$. The first expression divided by the second provides the dimensionless ratio known as the Reynolds Number:

(Eq. 2-13)

$$Re = \frac{Lv\varrho}{\mu}$$

Where:

Re = *Reynolds Number*

L = *characteristics system dimension*

v = *fluid velocity*

ϱ = *fluid density*

μ = *fluid viscosity*

The linear dimension, *L*, is a length characteristic of the flow system. It is equal to four times the mean hydraulic radius, which is the cross-sectional area divided by the wetted perimeter. Thus, for a circular pipe, *L* is the pipe diameter (*D*) and the Reynolds Number (sometimes termed the Flow Reynolds Number) takes the form:

(Eq. 2-14)

$$Re = \frac{Dv\varrho}{\mu}$$

Reynolds Number in this form is used to distinguish between laminar and turbulent flow. In *laminar flow*, the fluid is constrained to motion in layers, or laminae, by the action of viscosity. These layers of fluid move in parallel paths that remain distinct from one another (i.e., no mixing of molecules between layers). Laminar flow occurs when the Reynolds Number is less than about 2,000. In *turbulent flow*, the fluid is not restricted to parallel paths but moves forward in a random, chaotic manner. Fully turbulent flow occurs when the Reynolds Number is greater than about 3,000. Between Reynolds Numbers of 2,000 and 3,000, the flow may be laminar or turbulent, depending on the flow system conditions. Pipe or duct vibration, for example, can cause turbulent conditions to exist at Reynolds Numbers significantly below 3,000.

Another form of Reynolds Number is the Particle Reynolds Number. Here, the characteristic system dimension is the particle diameter, d_p, and the velocity, v_p, and describes the particle velocity relative to the gas stream:

(**Eq. 2-15**)

$$Re_p = \frac{D_p v_p \varrho}{\mu}$$

The Particle Reynolds Number is used to characterize flow conditions when particles move through or with a flowing fluid. Particle Reynolds Numbers less than about one indicate laminar conditions and define what is commonly termed the *Stokes Region.* Values over about 1,000 indicate turbulent conditions and define what is commonly termed the *Newton Region.* Particle Reynolds Numbers between 1 and 1,000 indicate transitional conditions. Most particle motion in air pollution control devices occurs in the Stokes and Transitional Regions.

Reynolds Number determination for flow conditions and particle behavior may be important considerations when designing air sampling equipment and instrumentation, but it is generally not of concern if the equipment is being utilized within its design parameters. For example, an impactor may be designed to capture particles which are < 2.5 μm, as an aerodynamic diameter, at a flow rate of 16.7 liters per minute. If the flow rate differs appreciably from the design flow rate, the size of the particles being captured will be altered as well. The concepts of Flow and Particle Reynolds Numbers are also important to the design and evaluation of air pollution control equipment and are discussed in more detail in EPA Course 413, Control of Particulate Emissions. The Flow Reynolds Number as it relates to cyclonic flow determinations is a topic of discussion in EPA Course 450, Source Sampling for Particulate Emissions.

2.6 Summary of Useful Equations

Temperature

$$°C = (°F - 32)/1.8$$

$$°F = 1.8°C + 32$$

$$K = °C + 273$$

Where:

$°F$ = *degrees Fahrenheit*
$°C$ = *degrees Celsius*
K = *degrees Kelvin*

Pressure

$$P = P_b + p_g$$

$$P = \varrho_f \left(\frac{g}{g_c} \right) h$$

$$\varrho_{f(1)} h_{f(1)} = \varrho_{f(2)} h_{f(2)}$$

$$1\,std\,atm = 29.92\,in.\,Hg = 760\,mm\,Hg$$

Where:

P = *absolute pressure*
p = *pressure*
ϱ = *density*
h = *pressure-head or height*
g = *gravitational acceleration*
g_c = *dimensional constant*

Subscripts:

g = *gauge*
f = *fluid*
b = *barometric or atmospheric*

Ideal Gas Law

$$PV = nRT$$

$$PV = \frac{m}{M}RT$$

$$R = \left(\frac{0.08205(liters)(atm)}{(g\text{ - }mole)(K)}\right) = \frac{62.4\,(liters)(mm\ Hg)}{(g\text{ - }mole)(K)}$$

1 g-mole = 22.414 *liters at* 273 *K and* 760 *mm Hg (molar volume)*

Where: P = *absolute pressure*
V = *volume*
m = *mass*
M = *molecular weight*
R = *gas constant*
T = *absolute temperature*
n = *number of g-moles of a gas*

Gas Density

$$\varrho = \frac{PM}{RT}$$

Where: ϱ = *density*
P = *absolute pressure*
R = *gas constant*
T = *absolute temperature*
M = *molecular weight.*

Viscosity, μ

$$1\ cp = 6.72 \times 10^{-4}\ \frac{lb_m}{ft \cdot sec}$$

$$1\ poise = 1\frac{g}{cm \cdot sec}$$

$$1\ cp = 10^{-2}\ poise$$

Reynolds Number

$$Re = \frac{Lv\varrho}{\mu} = \frac{inertial\ force}{viscous\ force}$$

Where: ϱ = *density of the fluid (mass/volume)*
r = *velocity of the fluid*

g_c = *dimensional constant*
L = *a linear dimension*
μ = *viscosity of the fluid*
Re = *Reynolds Number*

2.7 Units of Measurements

Recommended Units

At the present time, air pollution personnel are confronted with a multitude of confusing and conflicting units of expression. A search through the literature has shown a wide variation in the methods of reporting data. Many of the units of expression are carryovers from other fields, such as water pollution studies and industrial hygiene surveys. While these methods of expression are correct, their application to air pollution studies is often misleading. This section of the manual covers the units presently being used and those recommended for the more commonly measured air pollution parameters.

The recommended units were selected so that the reported values would be small whole numbers in the metric system. If possible, the reported units should be the same as those that are actually measured. For example, weight should be reported in grams or milligrams, and volume in cubic meters. The measured value should never be multiplied by large numbers to extrapolate to extremely large areas or volumes. If this is done, the resulting values are misleading. For example, to report particulate fallout on a weight per square mile basis, the area actually sampled, which is about 1 square foot, would have to be extrapolated to a square mile by multiplying the measured results by almost 28,000,000. Reporting the results on the basis of a square mile is misleading, because we are saying that the 1 square foot that we sampled is representative of a square mile surrounding this sampling site. This we know, in most cases, is not true.

When reporting results, the type of sampling instrument should be described, and when volumes of air are sampled, the temperature and pressure at the time of the sampling should be reported.

Table 2-1. Measurement units.

Parameter	Units in use	Unit recommended	Typical range
Particle fallout	Tons per square mile per month Tons per square mile per year Pounds per acre per month Pounds per acre per year Pounds per thousand square feet per month Ounces per square foot per month Grams per square foot per month Grams per square meter per month Kilograms per square kilometer per month Grams per month per 4-inch or 6-inch jar Milligrams per square inch per month Milligrams per square centimeter per time interval	mg/cm^2/mo (or yr)	0.5 to 135 mg/ cm^2/mo
Outdoor airborne particulate matter	Milligrams per cubic meter Parts per million by weight Grams per cubic foot Grams per cubic meter Micrograms per cubic meter Micrograms per cubic foot Pounds per thousand cubic feet	μg/m^3 (std)	10 to 5000 μg/ m^3 as TSP 30 to 140 μg/ m^3 as PM$_{10}$[1] 5 to 20 μg/ m^3 as PM$_{2.5}$ [1]
Gaseous materials	Milligrams per cubic meter Micrograms per cubic meter Micrograms per liter Parts per million by volume Parts per hundred million Parts per billion by volume Parts per trillion by volume Ounces per cubic foot Pounds per cubic foot Grams per cubic foot Pounds per thousand cubic feet	ppm or ppb by volume or μg/m^3 (std)	Parts per trillion to parts per million – –
Standard conditions for reporting gas volumes	760 millimeters Hg pressure and 20°C 760 millimeters Hg pressure and 0°C 760 millimeters Hg pressure and 65 °F 760 millimeters Hg pressure and 25°C 700 millimeters Hg pressure and 0°C 700 millimeters Hg pressure and 20°C 30 inches of mercury pressure and 65°F	760 mm Hg and 25°C	– –
Particle counting	Number per cubic meter of gas Number per liter of gas Number per cubic centimeter of gas Number per cubic foot of gas	Number of particles/m^3 of gas	10 million and above particles/m^3

---

[1] Based on National Trends data for PM$_{10}$ & PM$_{2.5}$.

Particle count in sedimentation devices (horizontal and vertical)	– –	Number of particles/cm²/ mo (or yr)	– –
Temperature	Degrees Celsius Degree Fahrenheit	°C	– –
Time	12:00 a.m. to 12:00 p.m. 0000 to 2400	0000 to 2400 (military time)	– –
Pressure	Atmospheric pressure Atmospheres Millimeters of mercury Inches of mercury Sampling pressure Millimeters of mercury Inches of mercury Millimeters of water Inches of water	mm Hg	– –
Sampling rates	Cubic meters per second Cubic meters per minute Cubic feet per second Cubic feet per minute Liters per second Liters per minute Cubic centimeters per second Cubic centimeters per minute	m^3/min. liters per minute	L/min to 3 m^3/min
Visibility	Miles and fractions of a mile Kilometers and fractions of a kilometer	km	– –

Conversion Problems

Sample Gas Problem

Discussion: The expression parts per million is without dimensions, i.e., no units of weight or volume are specifically designated. Using the format of other units, the expression may be written:

$$\frac{\text{parts}}{\text{million parts}}$$

"Parts" are not defined. If "cubic centimeters" replace "parts," we obtain:

$$\frac{\text{cubic centimeters}}{\text{million cubic centimeters}}$$

Similarly, we might write pounds per million pounds, tons per million tons, or liters per million liters. In each expression, identical units of weight or volume appear in both the numerator and denominator and may be cancelled out, leaving a dimensionless term.

An analog of parts per million is the more familiar term "percent." Percent can be written:

$$\frac{\text{parts}}{\text{hundred parts}}$$

To convert from parts per million by volume, ppm (μL/L), it is necessary to know the molar volume at the given temperature and pressure and the molecular weight of the pollutant. At 25°C and 760 mm Hg, one mole of any gas occupies 24.46 liters.

Convert the following: 2.5 ppm by volume of SO_2 was reported as the atmospheric concentration.

a. What is this concentration in micrograms (μg) per cubic meter (m^3) at 25°C and 760 mm Hg?
b. What is the concentration in $\mu g/m^3$ at 37°C and 752 mm Hg?

Solution: Let parts per million equal μL/L, then 2.5 ppm = 2.5 μL/L. The molar volume at 25° and 760 mm Hg is 24.46L, and the molecular weight of SO_2 = is 64.1 g/mole.

a. $$\frac{2.5\mu L}{L} \times \frac{1\mu\text{mole}\,*}{24.46\mu L} \times \frac{64.1\mu\text{g}}{\mu\text{mole}} \times \frac{1000L}{\text{m}^3} = 6.5 \times 10^3\ \frac{\mu\text{g}}{\text{m}^3}\ \text{at STP}$$

*Since, at STP, 1 mole of a gas occupies 24.46 liters, 1 μmole = 24.46 μL.

b. $$(24.46\mu L)\left(\frac{310\,\text{K}}{298\,\text{K}}\right)\frac{760\,\text{mm Hg}}{752\,\text{mm Hg}} = 25.73\mu L$$

$$\frac{2.5\mu L}{L} \times \frac{1\mu\text{mole}}{25.73\mu L} \times \frac{64.1\mu\text{g}}{\mu\text{mole}} \times \frac{1000L}{\text{m}^3} = 6.2 \times 10^3\ \frac{\mu\text{g}}{\text{m}^3}\ \text{at 37°C, 752 mm Hg}$$

This sample problem also points out the need for reporting temperature and pressure when the results are presented on a weight-to-volume basis.

Problems

1. Convert the following:
   a. 68°F – °C (answer: 20°C)
   b. 28°C – K (answer: 301 K)
   c. 29.03 in. Hg – mm Hg (answer: 737.3 mm Hg)

2. An ideal gas occupies a volume of 2000 mL at 700 mm Hg and 20°C. What is the volume of the gas at STP? (answer: 1874 mL)

3. If a concentration of carbon monoxide (CO) is noted as 10 ppm, what is this concentration in terms of $\mu g/m^3$ at STP (CO = 28 g/mole)? (answer: 11,440 $\mu g/m^3$, 11.4 mg/m^3)

4. Ambient air was sampled at a rate of 2.25 liters per minute for a period of 3.25 hours at 19°C, 748 mm Hg. What volume of air was sampled at STP? (answer: 441 L)

5. Convert 1000 $\mu g/m^3$ SO_2 at STP to ppm (SO_2= 64 g/mole). (answer: 0.38 ppm)

Tables to use in this task appear in Appendix C of this manual.

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Chapter

3

This chapter will take approximately 2.5 hours to complete.

OBJECTIVES

Terminal Learning Objective

At the end of this chapter, the student will be able to identify, classify, and determine appropriate use of air measuring instruments.

Enabling Learning Objectives

3.1 Describe the relationship of air movers to other sampling system components and its classification.
3.2 Identify air mover selection criteria.
3.3 Define and classify pumps.
3.4 Describe the operation principle and driving force of ejectors.
3.5 Describe the principle of operation and sampling procedures of liquid displacers.
3.6 Describe the principle of operation and sampling procedures of air displacers.
3.7 Identify flow rate control.
3.8 Identify flow rate for sampling.
3.9 Identify air measuring instruments.
3.10 Identify the seven volume meters that are commonly used in air sampling and analysis.
3.11 Describe rate meters.
3.12 Identify and describe velocity meters and their standard procedures.
3.13 View sample problems.
3.14 Describe $PM_{2.5}$ flowmeters and devices.

Air Measuring Instruments

The ultimate goal of atmospheric sampling is to extract a sample, representative of a constituent of interest (pollutant) present in the environment, to determine its concentration. In order to determine a pollutant concentration, the mass of the pollutant and the volume of air sampled must be known.

The discussion in Chapter 3 is divided into two major sections: air movers and air measuring devices. Air movers are responsible for drawing the sample gas through the sampling train. Air measuring devices provide an accurate measure of the rate of gas flow (e.g., liters per minute, cubic feet per hour) or volume (e.g., liters, cubic feet) over a measured time period (e.g., minutes, hours) through the sampling train. The volume of air sampled, measured directly or indirectly, and the mass of pollutant collected (discussed in Chapters 4 and 5) are used to determine the concentration of the pollutant.

3.1 Introduction to Air Movers

The primary purpose of an air mover in the sampling process is to create a flow of air that will allow the contaminant in the air to be analyzed directly or to be captured by a collection device for subsequent analysis. Air movers include pumps, ejectors, and liquid and air displacement devices. Collection devices include filters, adsorbers, impingers, and impactors. Air movers range in capacity from a few cubic centimeters per minute (cm^3/min) of air up to tens of cubic meters per minute (m^3/min). In operational complexity, air movers range from a squeeze bulb to a multistage pump. Regardless of the type of air mover selected, they all move air through the sampling train by creating a pressure differential in the system. Air moves in a closed system, such as a sampling train or in the ambient air, only if there is a change in pressure from one location to another.

Relationship of Air Movers to Other Sampling System Components

Air movers are vital components of sampling trains used for the sampling and analysis of air for its pollutant content (see Figure 3-1). Several of the considerations governing the selection of an air mover for a particular application will be mentioned in this discussion.

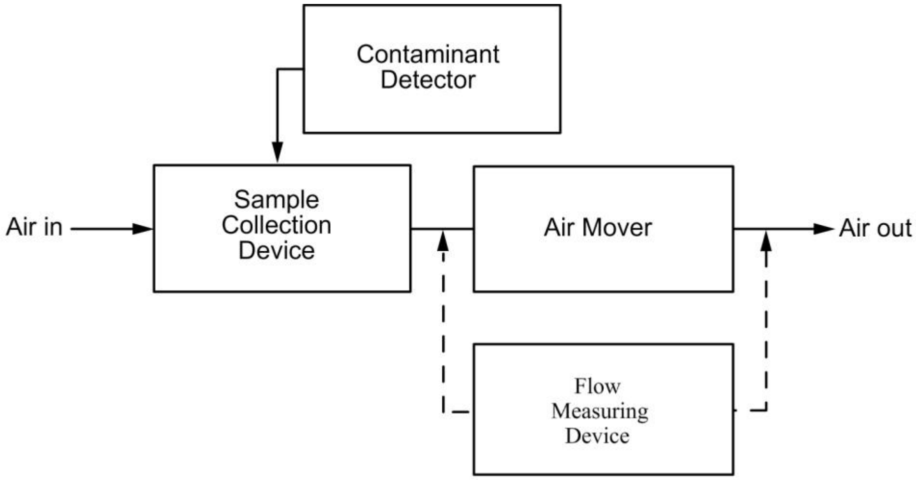

Figure 3-1. A sampling train.

Air Mover Classification

There are many parameters by which air movers can be evaluated and classified. Classification of air movers can be made according to their function, capacity, "driving" force, and principle of operation, among other parameters. The classification scheme often depends to a great extent on the classifier. The actual types of air movers to be discussed in this text are *pumps, ejectors, liquid displacers,* and *air displacers.*

3.2 Air Mover Selection Criteria

Since there is no one "typical" air sampling train, equipment selection is an important aspect of any airborne sampling scheme, meaning that air mover selection must be made along with the selection of other sampling train components. Here are some of the many factors to be considered before selection is discussed. The itemizing of the considerations is not necessarily in order of their importance.

Pollutant Concentration and Sampling Time

The required flow rate of the air mover is often determined by the sensitivity of the analysis method, which in turn sets the minimum quantity of the contaminant required for analysis. For example, if the analysis procedure required 10 µg of material to obtain the desired precision, and if the air contains 1 $\mu g/m^3$ of that material, a sample size of 10 m^3 would be required, assuming 100% collection efficiency. The required flow rate of the air mover can be calculated by determining the available sampling time and the sample volume required. For example, if the above-mentioned 10 m^3 of air had to be moved (sampled) in a period of 10 hours, an air mover of 1 m^3/hr capacity could be used. In many instances it is more feasible to sample for longer periods of time, and sometimes at higher rates, than those required. As long as the sample size is greater than the minimum detectable and less than the concentration that theoretically saturates the collection medium, this may be of no consequence.

When whole air sampling is conducted, such as sampling into an inert bag or evacuated canister, the sampling flow rate determines the degree to which the sample represents the true concentration on a temporal basis. Therefore, it is important to understand the temporal variations associated with the constituent being sampled and to adjust the sampling time accordingly. These days, "whole air" sampling is often conducted in conjunction with sampling for air toxics.

Sampling Rate Required

In some instances it may be necessary to sample at some required flow rate to ensure efficient sample collection. An example is the collection of a sample by using a chemical reaction. The reaction kinetics may depend on the length of time the contaminant is in the presence of the reacting substance, and the length of contact time is dependent on the sampling rate. Another example would be the collection of particulate matter by using an impinger or impactor. For example, collection of a sample at a low flow rate should increase the time that the air is in contact with the reagent and may also decrease the size of the bubbles, thus increasing the surface area of air in contact with the reagent. The particle size collected will be dependent on the approach velocities, and these in turn are dependent on the sampling rates.

Physical and Chemical Nature of Air to be Sampled

The operation of the air mover selected must be compatible with the physical and chemical characteristics of the air and contaminant to be sampled. Air of a corrosive or abrasive nature can create problems with the air mover unless the internal parts are nonreactive with the sample air.

In instances where sampling is to be done in a potentially explosive environment, approved explosion-proof air movers or explosion-sealed air movers should be selected. A completely sealed electric motor for a pump, in conjunction with non-sparking metal parts, is an example of an explosion-sealed air mover.

Portability of Air Mover

Air sampling is often performed at temporary sampling sites. When sampling trains must be moved from location to location, it is important that each component be as portable and lightweight as possible. At permanent sampling locations, air mover portability is not such an important consideration.

The power source for the air mover may be the limiting factor in its portability, especially when the power source must be AC line voltage.

Air Mover Noise

Since air sampling may be required in areas having noise restrictions, the noise produced by an air mover must be considered. Also, the suppression of air mover noise has aesthetic value. Noise levels may be considered in relation to the length of the sampling period; that is, for short periods high noise levels *may* be acceptable. Many commercially available air movers have special sound-adsorbing liners, vibration-reducing cushioning material, or mufflers as noise-reducing components of the mover itself.

Air Mover Maintenance

Manmade equipment, whether air sampler components or computers, will not be maintenance-free. Maintenance considerations are of special importance for equipment to be used in the field, because valuable time can be lost in transit between the repair shop and the sampling location. There are three particular points to consider about air mover maintenance: (1) air mover parts that might need repairing should be easily accessible; (2) the complete repair should not be very time consuming; and (3) air mover parts should not be overly expensive. In general, increasing preventive maintenance activities decreases air mover malfunctions.

Resistance

Flow resistance considerations may dictate the selection of an air mover of a particular type (see Figure 3-2). The sample collection device will offer some resistance to the flow of air through it; therefore, the air mover must be able to overcome this resistance for efficient sample collection.

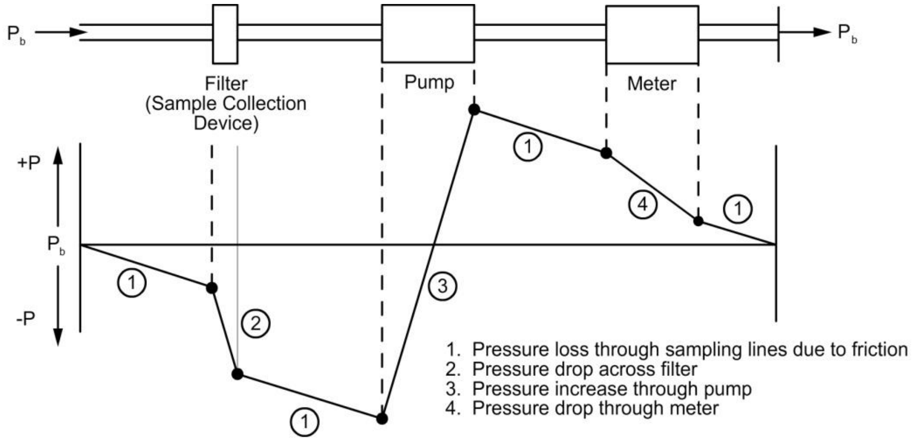

Figure 3-2. Pressure profile for basic sampling apparatus.

Constant Flow Rate

It is often desirable to collect a sample at a constant flow rate. Variation in sample conditions or other external influences can make this difficult. For example, the resistance of a filter can be expected to increase with sample "buildup," thereby decreasing the flow rate through the sample apparatus. Poor voltage regulation can result in variable motor speeds, leading to variable sampling rates. However, some commercially available air movers feature constant flow rates despite varying sampling conditions; others require flow regulation devices in order to have constant flow rates. Some flow regulation mechanisms will be discussed later in the chapter. Another factor of importance in some applications is the ability to vary the flow rate of the air mover and then to maintain constancy at the selected rate. This topic will also be discussed in more detail later.

3.3 Pumps

Definition and Classification

Pumps have been defined as devices that raise or transfer fluids. Since air is a fluid, a pump that moves air either raises it to another level or transfers it to another location. In air sample collection, the air is transferred from one location through, or into, a sample collection device.

Classification of pumps is a difficult task because of the many variables. This section will discuss pumps in terms of two broad classes based on flow variation with pressure. These two major classes will be subdivided into categories according to specific principles of operation: (a) *positive displacement pumps* and (b) *centrifugal pumps*.

Positive Displacement Pumps

Positive displacement pumps are often characterized by a linear relationship between the suction pressure and pump capacity (see Figure 3-3). This indicates that $\Delta Q/\Delta p$ (ΔQ is the change in flow rate; Δ p is the pressure drop across the pump) is a constant value. Figures 3-3 and 3-5 are representative of characteristic curves of pumps to be discussed later.

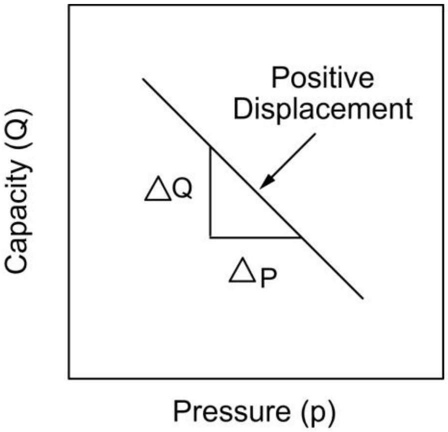

Figure 3-3. Positive displacement pump.

The name "positive displacement" arises from the fact that the inner parts of these pumps are movable and tight-fitting, and the air is displaced through them by the movement (displacement) of these tight parts. Figure 3-4 indicates a further subdivision of positive displacement pumps, this division being made according to the principle of operation. Reciprocating pumps are characterized by fixed casings containing movable pistons that work only forward-and-backward or up-and-down and by the pressure of suction and discharge valves.

Principle Operation	Type of Pump
Reciprocating	Piston Plunger Diaphragm
Rotary (not discussed in this manual)	Gear Lobe Vane Screw Rotary Plunger

Figure 3-4. Classification of positive displacement pumps.

Piston Pump (Reciprocating)

In a piston pump, air is drawn into a chamber or grinder on the suction stroke of a piston and is then pushed out on the discharge stroke, as illustrated in Figure 3-5. On the suction stroke, the suction valve is open, allowing air to flow in; on the discharge stroke, the suction valve closes and the discharge valve opens, allowing air to flow out. An internal combustion engine is an example of a piston pump. Piston pumps vary in complexity of operation from manually operated ones to models with many working parts.

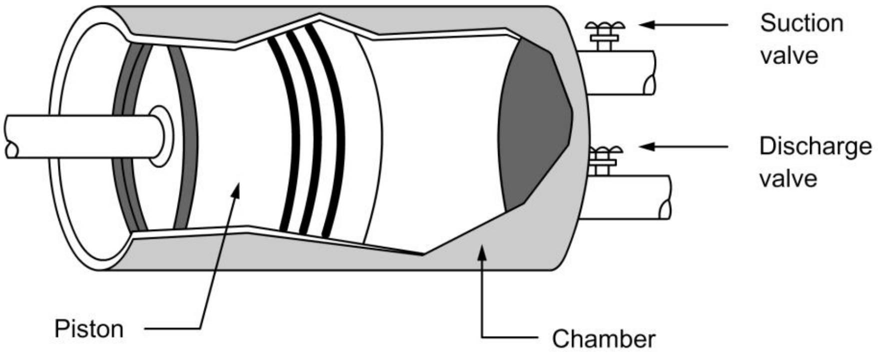

Figure 3-5. Piston pump.

Diaphragm Pumps (Reciprocating)
In principle, the operation of a diaphragm pump is very similar to a piston pump. The piston (plunger) in a diaphragm pump does not move in a tightly fitted chamber as in the piston pump, but is attached to the center of a circular diaphragm, the outer edge of which is bolted to a flange on the pump casing. The diaphragm may be made of metal or some soft material such as Teflon® or neoprene. The most important characteristics of the diaphragm material are its flexibility and resistance to reaction with the air being moved. The up-and-down motion of the plunger is permitted by diaphragm flexibility without the rubbing of one part on another (see Figure 3-6). On upward movement of the plunger, air flows into the pump through a suction valve. Downward movement of the plunger closes the suction valve and the air is forced through a discharge valve, perhaps located in the plunger itself. An automobile fuel pump is an example of a diaphragm pump.

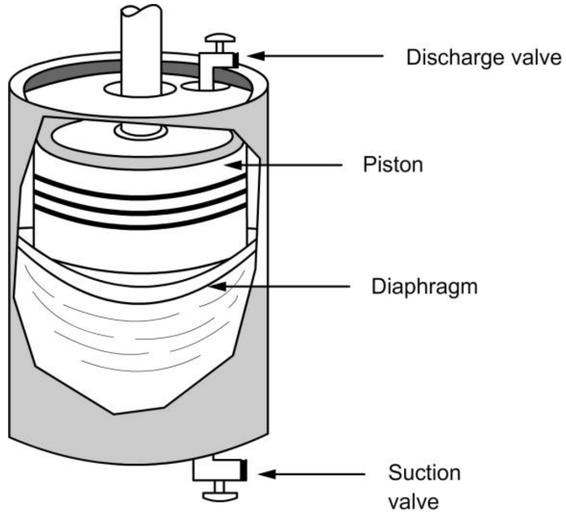

Figure 3-6. Diaphragm pump.

Centrifugal Pumps

Centrifugal pumps are representative of pumps other than positive displacement pumps. Centrifugal pumps do not have a straight line relationship between suction pressure and capacity; thus, $\Delta Q/\Delta p$ is not constant (see Figure 3-7).

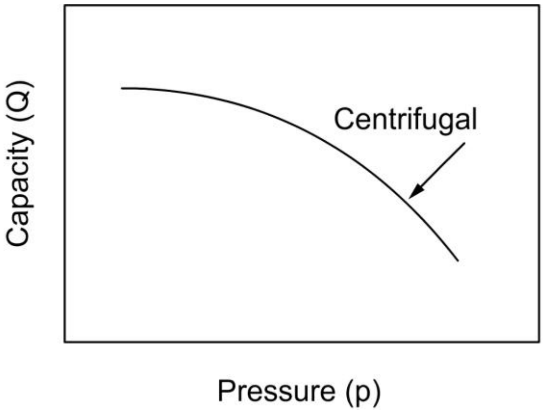

Figure 3-7. Centrifugal pump.

A centrifugal pump moves fluids by a centrifugal force created by a wheel, called an impeller, revolving in a tight casing. Some additional examples of pumps other than positive displacement pumps are: (a) turbine pumps, (b) propeller pumps, and (c) screw drag pumps. Each of these exhibits the same general pressure-capacity relationship as the centrifugal pump.

Centrifugal pumps (or fans) employ centrifugal force to move air. The simplest form of this type of pump consists of an impeller routing in a volute ("snail's shell") casing (see Figure 3-8). The rotation of the impeller creates a decreasing pressure at the impeller "eye," causing air to be drawn into the pump. Air drawn into the center of the impeller is "picked up" by the vanes and accelerated to a high velocity by rotation of the impeller. It is then discharged by centrifugal force into the casing and out the discharge nozzle.

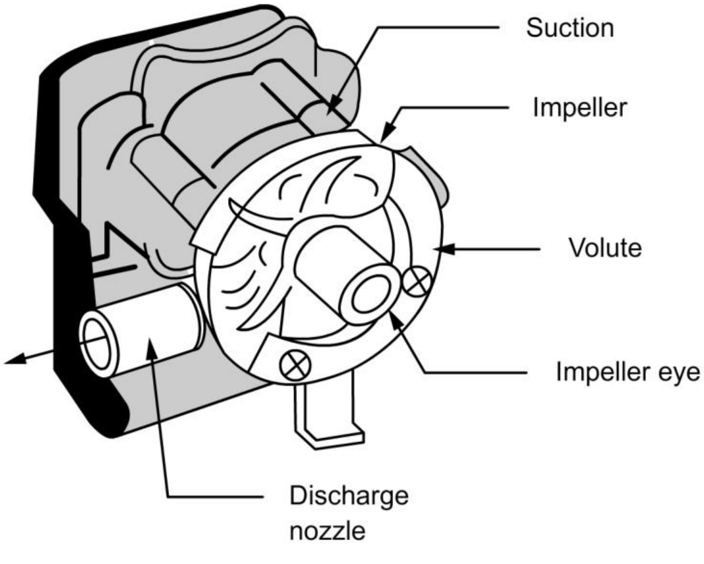

Figure 3-8. Centrifugal pump operation.

Centrifugal pumps encountered in air sampling can be divided primarily into three categories: (a) radial flow, (b) axial flow, and (c) mixed flow. Centrifugal pumps may also be classified into single-stage or multistage. Single-stage indicates a pump in which the total head is developed by one impeller; multistage indicates a pump having two or more impellers acting in series in one casing.

"Driving Forces" for Pumps

All pumps have at least one common characteristic - they have movable parts. The movement of the parts is the basis for the transfer of the particular fluid of interest. For the parts to move there must be a "driving force." Driving forces for pumps can be categorized as: (a) manual and (b) motors.

Some air movers in the general category of pumps can be operated manually. A hand-operated hypodermic syringe (piston pump), a hand-cranked pump (e.g., Drager Pump, MSA Midget Impinger Sampler), and a tire pump using a foot pedal are examples. These types of air movers are rarely used today. Electric motors operated by commercial power, motor-generation sets, or batteries are all used for driving air sampling pumps. When using batteries as the driving force, several factors should be considered, such as the motor power requirements and the required length of sampling. The length of the sample time is important in relation to the life of the battery.

In instances where constant flow is required, it is important that the driving force for the pump is constant and not be affected by environmental factors. If the driving force is variable, measures may have to be taken to try to regulate it. For example, a voltage regulator may be required in conjunction with an electric motor that is driving an air pump where variable voltage power sources are encountered.

Characteristic Curves

Pumps perform differently under different conditions; therefore, "characteristic curves," showing the relationships between the various conditions affecting their performance, are usually supplied by the manufacturer. The characteristic curves of most interest in air sampling are those indicating the pressure-flow relationship (see Figures 3-9 and 3-10).

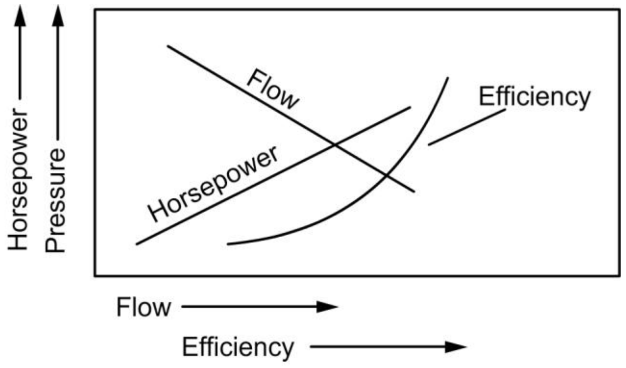

Figure 3-9. Characteristic curve for a positive displacement pump.

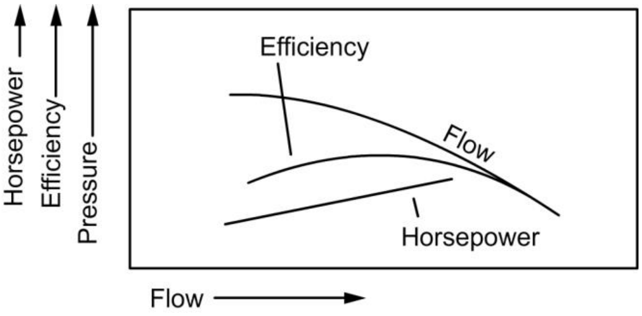

Figure 3-10. Characteristic curve for a centrifugal pump.

The quantity of flow is usually expressed in terms of a flow rate - e.g., cubic feet per minute (cfm), liters per minute (lpm), and cubic feet per hour (cfh). The pressure represents the amount of suction that must be available to overcome the resistance of the air to movement through the sampling train. Pressure can be expressed in pounds per square inch gauge (psig) or in inches of an equivalent height of a fluid. The suction pressure at which a pump is required to operate is often referred to as its head. The total head is equal to the total pressure drop between intake of the sample collection device and the pump intake. Other parameters such as efficiency, horsepower, and speed are indicated in the characteristic curves for certain pumps. Empirical equations relating various parameters are also available. It should be noted from Figures 3-9 and 3-10 that different types of pumps possess different characteristics. As flow increases for a rotary pump, the efficiency increases; as flow increases for a centrifugal pump, the efficiency increases and then decreases.

Selecting a Pump

When choosing a pump, the sampling rate required may limit the selection to certain categories of air movers. On the other hand, if flow rate is not critical, the wide variety of air movers available may require a more involved evaluation. A comparison of some of the advantages and disadvantages of certain types of pumps is found in Figure 3-11.

Pump type	Advantages	Disadvantages
Piston pump (reciprocating)	1. Can operate at high suction pressure 2. Can be metered	1. Small capacity 2. Seal required between piston & piston chamber 3. Working parts such as check valves and piston rings may cause difficulties 4. Pulsating flow 5. Moderate maintenance
Diaphragm pump (reciprocating)	1. Wide range of capacities 2. No seal required 3. Good in continuous operation	1. Limited materials of construction 2. Operation at limited suction pressures 3. Pulsating flow 4. Periodic diaphragm replacement 5. Moderate maintenance
Centrifugal pump	1. Large range of capacities 2. No close clearance 3. Can obtain high suction heads by multistages 4. Light maintenance	1. No small capacities 2. Turbulence 3. Operational noise

Figure 3-11. Pump comparison.

Many features of commercially available pumps may or may not warrant consideration. Some features may have direct applicability for certain uses; others may provide flexibility, making the pumps more generally usable. In this discussion, only gauges and continuous operation capability will be considered.

Pump Gauges

Many pumps have inlet vacuum gauges and/or outlet pressure gauges. These gauges, upon proper calibration, can be used to determine the approximate flow rate through the pump. The flow rate can be determined by use of the pump's characteristic curve for the pressure-flow relationship (see Figure 3-12), or by direct reading if the gauge is calibrated in terms of cfm on its dial.

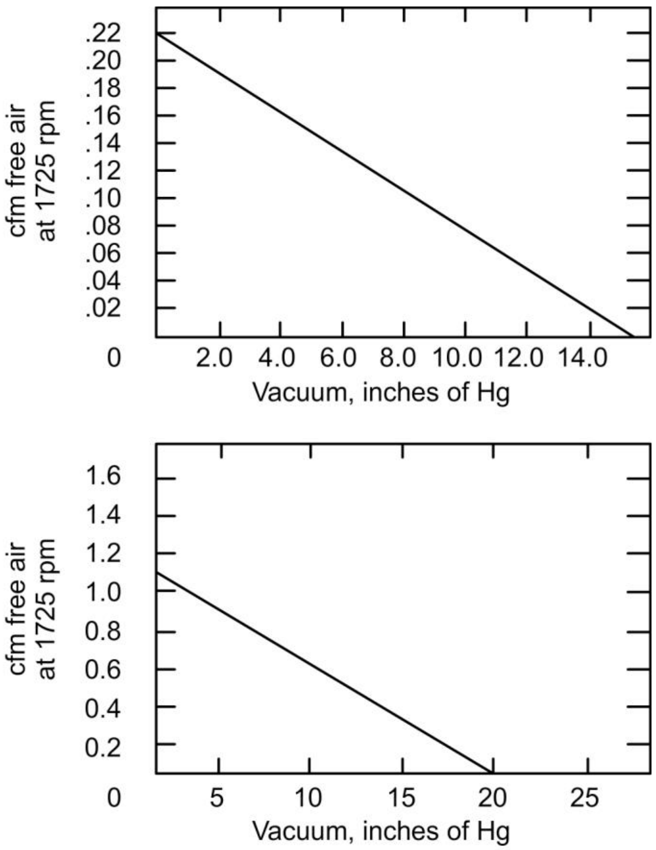

Figure 3-12. Pressure-flow relationship for metal bellows pumps for vacuum (continuous operation capability).

Pumps are often required to operate continuously for long periods of time (hours to days) at high vacuum. Some pumps such as rotary or diaphragm pumps used in ambient air monitors are capable of continuous operation at high vacuum, while others would tend to "burn" themselves out. The importance of this capability would be dependent on the sampling time required.

3.4 Ejectors

Principle of Operation

Another classification of air movers is the ejector, also known as an aspirator. As depicted in Figure 3-13, ejectors operate according to the jet principle. At the nozzle, the pressure head of the driving force is converted into a high velocity stream. The passage of the high velocity stream through the suction chamber creates a decreased pressure (vacuum), thus drawing air into the chamber itself. The incoming air is mixed with the high velocity driving force mixture and can be ejected against moderate pressure through the diffuser.

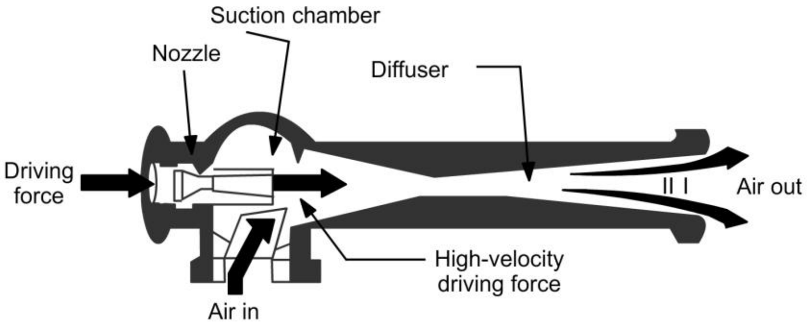

Figure 3-13. Ejector operation.

Driving Forces

The pressurized fluid that is converted into a high velocity jet stream in an ejector may be of several types. Some examples of fluids used are water, steam, compressed air or CO_2, and other gases such as Freon. Freon is no longer used since it has been classified as an ozone-depleting substance.

Sampling Use of Ejectors

Using ejectors as samplers, air moved is adequate for lower sampling rates. The sampling rates vary from a few liters per minute up to several cubic feet per minute. The flow rate through an ejector can be regulated to some extent by adjusting the nozzle opening. One limitation of using ejectors is that the pressurized driving force may have a time limit on its available effectiveness (i.e., if a pressurized gas cylinder is used, it may last only for a limited amount of time).

3.5 Liquid Displacers

Principle of Operation

Air movers that operate according to the principle of liquid displacement incorporate two sampling train components into one entity. In this case, the liquid displacement unit serves as both the sample collection device and the air move, or it may provide the air-moving capability for a second device which may act as the sample collection device.

Gravity flow of liquid from a container creates a vacuum within the container, thus drawing air into the container to fill the displaced volume (see Figure 3-14).

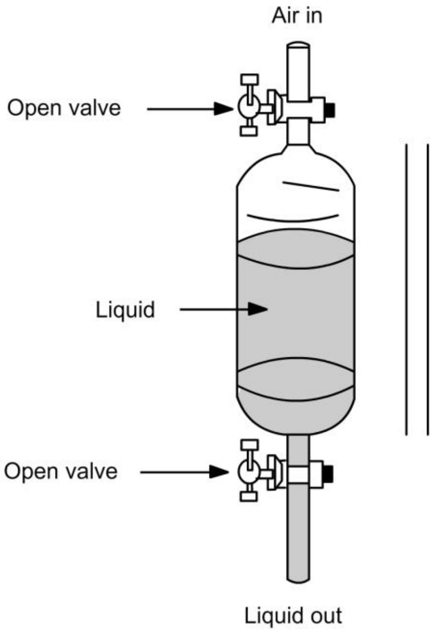

Figure 3-14. Liquid displacement.

Sampling by Use of Liquid Displacement

Liquid displacement is usually used only for grab sampling. The sample volume capacity is limited to the size of the liquid container. Some examples of liquids used are water, mercury (Hg), and organic solvents. These devices are generally no longer used as air sampling devices; however, they are used to calibrate volume air measuring devices, such as wet test meters. This technique is discussed in detail later in this chapter. In addition, students will calibrate a wet test meter using liquid displacement during the laboratory exercise portion of this course.

3.6 Air Displacers

Air displacement operates by the simple displacement of air or the creation of a vacuum in a closed container. Evacuated flasks and "plastic" bags are examples of air displacers.

Evacuated Flasks: Principle of Operation

A flask is evacuated by a vacuum pump to a very low pressure that must be determined. The flask is sealed and transported to the sampling location. When a valve is opened on the flask, the surrounding air moves into the flask because of the pressure differential. On closing the valve, the sample is confined for subsequent analysis. The rate at which sample air is permitted to enter the evacuated flask may be varied and is often prescribed by a sampling method designated for a particular constituent or classification of constitutents.

Sampling by Use of Evacuated Flasks

Evacuated flasks are usually used only for grab sampling; consequently, only relatively small sample volumes can be collected. Grab sampling is discussed in detail in Chapter 5.

Sampling methods for air toxics, such as TO-14A for the determination of volatile organic compounds (VOCs), specify the use of polished stainless steel canisters evacuated to a pressure less than 0.05 mm Hg, on an absolute basis. 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.

The 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.

Careful consideration should also be given to the possibility of flask "implosion" when glass containers are used, and appropriate protective means should be undertaken. However, glass flasks are seldom used today.

"Plastic" Bags: Principle of Operation

Air moving by use of a "plastic" bag (i.e., Tedlar, Mylar, Teflon, aluminized PVC) is another example of an air displacer. Since a plastic bag is non-rigid by design, either it is mounted within a rigid, airtight outer container and filled by creating a slight vacuum in the space around the bag, or, if there is no rigid outside container, air is pumped directly into the plastic bag. To be precise, the plastic bag is not responsible for the movement of the sample air flow as is the case with an evacuated flask; it merely serves as a collection device to hold the sample gas for subsequent analysis.

Sampling by Use of "Plastic" Bags

Plastic bags are usually used only for grab sampling; consequently, only relatively small sample volumes can be collected. Grab sampling with the use of a plastic bag is discussed in detail in Chapter 5.

3.7 Flow Rate Control

Control by Diversion

The principle of flow diversion is simply that the air moved by the air mover is not all passed through the sample collection device. As depicted in Figure 3-15, a "bleed" valve control, typically integral to the air mover (pump), allows the variation of the actual flow through the sample collection device. The position of the flow measuring device is such that it measures only the flow passing through the sample collection device.

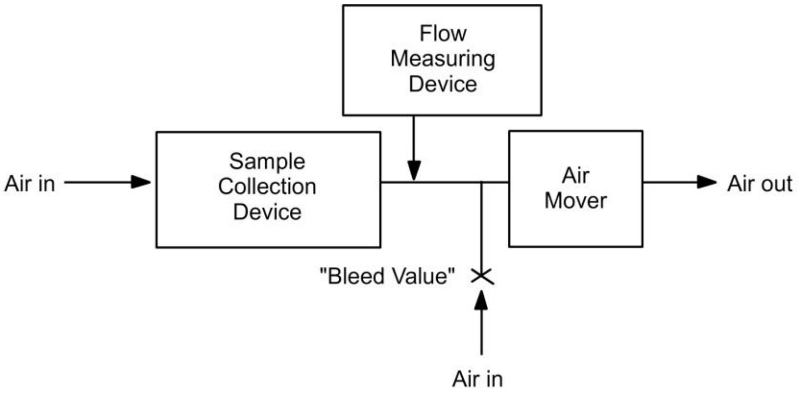

Figure 3-15. Flow rate control by diversion.

Resistance Control

In most air-moving devices, the flow rate decreases as the resistance it must overcome increases. Examples of this are depicted in Figures 3-9 and 3-10, which show sample characteristic curves for several pumps. The flow rate of the air mover can, therefore, be regulated by controlling the resistance it must overcome. A common method of control is to partially close a valve in the intake line, thus creating a greater resistance. Reproducible flow control can be accomplished by using needle valves with resettable marking.

Driving Force Control

It may be possible to control the air mover driving force, thereby controlling the rate of air flow. Adjustment of the nozzle opening on an ejector can be considered a driving force control because it affects the velocity of the pressurized gas stream. The velocity of the gas stream, in turn, affects the suction pressure.

Another example of driving force control is electric motor speed regulation. This can be accomplished on some pump motors by use of a variable transformer, which controls the amount of power sent to the motor. These variable transformers are known by several names, such as variacs and powerstats.

3.8 Flow Rate for Sampling

After a particular flow rate has been selected for sampling, and after it has been set for the sampling train, it is usually necessary to maintain the flow at exactly that rate.

Need for Control

A variation of the desired flow rate can be caused by a variation in the air mover driving force or a variation in the resistance to air flow. The resistance to air flow is equivalent to the suction head the pump must overcome. Some sampling conditions affecting flow variation have been mentioned above. Flow variation during sampling may affect more than the determination of the volume of air sampled; it may also affect the performance of the sample collection device. For example, the absorption rate of a bubbler may be altered by a variation of the flow rate through it.

Control Mechanisms

Many flow rate control mechanisms operate by keeping at a constant value the effective resistance that the pump must overcome. In other words, as depicted in Figure 3-16, the pressure drop (Δp) from the environment being sampled to the pump intake is held constant.

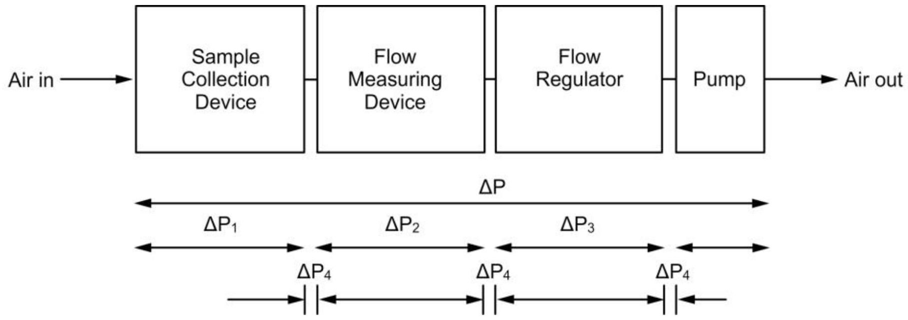

Figure 3-16. Flow rate control mechanism.

Sources of pressure drop in a system of this type include:

- the pressure drop across the sample collection device (Δp_1),
- the pressure drop across the flow measuring device (Δp_2),
- the pressure drop across the flow regulator (Δp_3), and
- the pressure drop due to friction in connecting lines (Δp_4).

Friction losses and flow measuring losses are usually considered as being constant. The resulting relationship can be shown in Equations 3-1, 3-2, 3-3, and 3-4.

(Eq. 3-1) $\varDelta p = \varDelta p_1 + \varDelta p_2 + \varDelta p_3 + \varDelta p_4$

(Eq. 3-2) $\varDelta p_2 + \sum \varDelta p_4 = constant$

(Eq. 3-3) $\varDelta p - \varDelta p_2 - \sum \varDelta p_4 = \varDelta p \ adjusted$

(Eq. 3-4) $\varDelta p_1 + \varDelta p_3$

Initially in the sample collection (assume for this discussion the collection device is a filter for the collection of particles), the sample collection device resistance ($\varDelta p_1$) is low; therefore, the regulator would have to offer a higher resistance ($\varDelta p_3$). As sampling proceeds, the sample collector resistance ($\varDelta p_1$) increases (as a “particle cake” builds up on the filter), thus automatically lowering the flow regulator resistance (Δp_2) and keeping Δp_{adj} at a constant value. The regulator resistance control may be actuated by several mechanisms, usually a pressure drop directly related to time rate.

Another type of control mechanism accomplishes control by varying the pump motor speed. As the pressure drop across the sample collection device increases, a switching arrangement increases the pump motor speed - thus drawing a constant air flow.

3.9 Air Measuring Instruments

Introduction

The accuracy and precision of a given method for the determination of the concentration of an air pollutant are based on two factors:

- the accuracy and precision of the sampling method, and
- the accuracy and precision of the analytical method.

Examine the following term:

(Eq. 3-5)

$$\frac{\mu g}{M^3}\left(\frac{\text{Mass of pollutant}}{\text{Volume of air sampled}}\right)$$

You can see that the μg (*mass of pollutant*) term is a result of the analytical process, while the M^3 (*volume of air sampled*) term is a result of the sampling process. Not only is the mass of pollutant important in the final calculation of $\mu g/M^3$, but the volume of air sampled is also important. We will concentrate in this section on the measurement of the volume of air sampled.

The accuracy and precision of the sampling method depend on these factors:

- the environmental conditions during sampling,
- the collection efficiency of the sampling method,
- the accuracy and precision of the flow rate measurement, and
- any interferences.

The determination of the volume of air sampled, V (e.g., liters), generally involves a measurement of flow rate, Q (e.g. liters/minute), and sampling time, t (e.g. minutes).

(Eq. 3-6)

$$V = Q \times t$$

Types of Air Measuring Devices

The flow rate during atmospheric sampling can be measured by a variety of air measuring devices. Air measuring devices can be broadly classified into three categories: *volume meters, rate meters,* and *velocity meters.*

Volume meters measure the total volume, V, of gas passed through the meter over some specified time period. If the time period, t, is measured with a timing device, flow rate can be calculated by:

(Eq. 3-7) $$Q = \frac{V}{t}$$

Rate meters measure the time rate of flow through them. Flow rate is measured through some property of the gas.

Velocity meters measure the linear velocity, v, of a gas in a duct. Volumetric flow rate can then be calculated by measuring the cross-sectional area, A, of the duct through which the gas is flowing, by:

(Eq. 3-8) $$Q = A \times \bar{u}$$

Calibration

Air that is to be sampled often is moved at a known rate over a known time period. The determinative process used to establish this known flow rate and known time period is a form of calibration. Remember that $V = Q \times t$, or that volume sampled, V, is the product of flow rate Q and time t. The calibration process applied to both the flow rate and time allows the accurate determination of volume.

In precise terms, calibration is the comparison of an output value with a known input value. It is typical to "challenge" an instrument under calibration with a series of values (e.g. concentrations, temperatures, pressures) for a given operating range. The difference between the input and output may be accounted for by making an adjustment to the device being calibrated. This is typical in modern instruments or devices. Alternatively, a calibration curve is developed to represent the difference by plotting the "known input value" versus the "instrument response value." If this approach is used, all subsequent data from that instrument will need to be adjusted based on the calibration curve.

The frequency with which calibration occurs depends on a number of conditions. Some of these are:

- instrument use (What are the conditions under which the instrument is used?),
- instrument users (How many different people use the instrument? What are their qualifications?),
- instrument characteristics (How often does the instrument require calibration under controlled laboratory conditions? How sensitive is the instrument?), and
- regulatory requirements as to how frequently the instrument or device must be calibrated.

The basic equipment required for calibrating air flow measuring instruments includes a standard meter, an air mover, and often a source of constant power.

Standard meters are of three types: primary standards, intermediate standards, and secondary standards. *Primary standards* are those whose volumes can be determined by measurement of internal physical dimensions alone. The measured internal dimensions are regular, and accuracies better than ± 0.30% can be achieved. *Intermediate standards* are devices which have an accuracy only marginally less than that of primary standards at $\leq$ 2%, but whose internal dimensions are not easily measured. *Secondary standards* are those calibrated against primary or intermediate standards under known conditions of gas type, temperature, and pressure. Accuracies less than 5% are generally achievable.

3.10 Volume Meters

Volume meters measure the volume of gas passing through the meter. When coupled with a timing device (like a calibrated stopwatch), flow rate (volume/time) can be calculated. There are seven volume meters commonly used in air sampling and analysis.

The Spirometer (or "Bell Prover") – Primary Standard

The spirometer consists of a cylinder of known volume, closed at one end, with the open end submerged in a circular tank of fluid (Figure 3-17). The cylinder can be opened or closed to the atmosphere by a valve. As the cylinder is lowered into the water, and the water displaces the air and causes it to be discharged from the cylinder, the rate of discharge can be regulated.

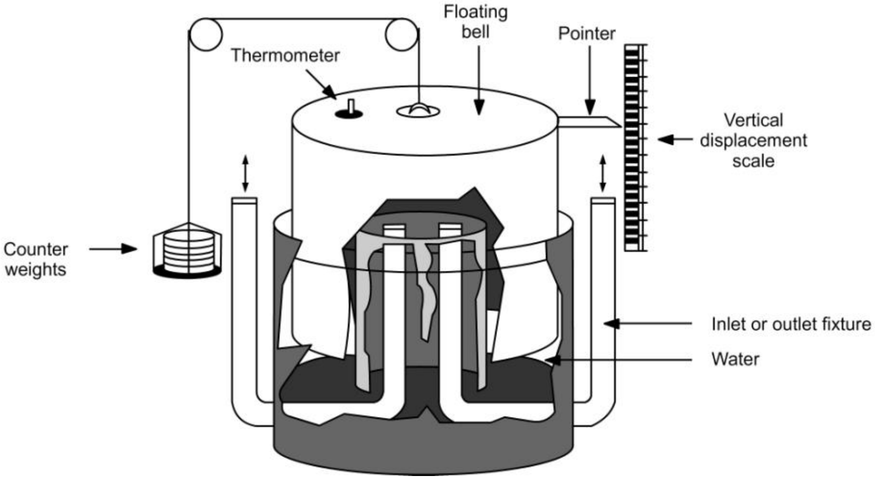

Figure 3-17. Spirometer.

The volume of the cylinder is determined from its dimensions. A counterweight and cycloid counterpoise allow pressure differentials across the spirometer as low as 0.02 inches of water (Figure 3-18).

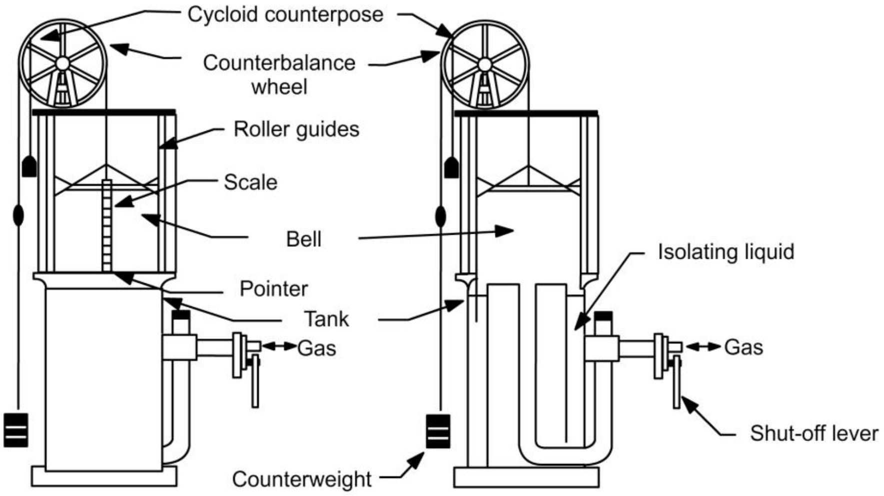

Figure 3-18. Orthographic and cross-sectional views of a 5-ft^3 spirometer.

The volume of air passed through a spirometer is given by the following formula:

(Eq. 3-9)

$$V = \frac{\pi d_2 h}{4}$$

Where: V = *volume of air passed through spirometer*
π = *a constant = 3.14*
d = *diameter of bell*
h = *vertical displacement of bell*

The fluid in the spirometer should be at the same temperature as the room. This is to ensure that the fluid and the air will be in thermal equilibrium and thereby minimize spirometer fluid evaporating into the air. This thermal equilibrium also simplifies volume corrections since temperature is constant during the calibration procedure. This is true for water, but some spirometers use oil. The real importance of thermal equilibrium is that the air displaced from the bell must be at the same temperature as the room for volume calculations. The pressure inside the bell is also brought into equilibrium with room conditions.

Once the volume of air is determined using room conditions, a conversion to standard conditions must be made to determine the true volume of air that has passed through the spirometer. EPA standard conditions for temperature and pressure (STP) generally applicable to atmospheric sampling and ambient monitoring are 25 degrees Celsius (298 K on an absolute basis) and 760 mm Hg, also on an absolute basis. This conversion to standard conditions is made using the following formula (see Equation 2-7):

(Eq. 3-10)

$$V_2 = V_1\left(\frac{P_1}{760\,\text{mm Hg}}\right)\left(\frac{298\,\text{K}}{T_1}\right)$$

Where:

V_2 = *volume of gas at* 2^{nd} *conditions or at* P_2 *and* T_2
V_1 = *a volume of gas at* 1^{st} *conditions of* P_1 *and* T_1
T_1 = *initial temperature of gas, K*
T_2 = *final temperature of gas (in this case, 298 K)*
P_1 = *initial pressure of gas, mm Hg*
P_2 = *final pressure of gas (in this case, 760 mm Hg)*

The spirometer is calibrated by the manufacturer against a National Institute of Standards and Technology (NIST) "cubic-foot" bottle. If a spirometer is suspected to be in error, its calibration can be checked with an NIST-certified "cubic-foot" bottle or by a "strapping" procedure.

The strapping procedure involves the measurement of the dimensions of the bell with a steel tape and subsequent calculation of the volume. Experienced personnel routinely obtain accuracies of ± 0.2% when calibrating a spirometer by the strapping procedure. Nelson (1972) gives a very detailed procedure for performing the strapping procedure. Manufacturers of spirometers include example calculations in the literature accompanying their instruments.

Flow rates can be measured by timing the volume of air passing to or from the spirometer and determining the rate of flow. The spirometer is simple, inexpensive, dependable, and is used almost solely as a primary standard for calibration of other types of flow- and volume-measuring devices. Because the spirometer can be produced in large sizes, it has typically been used to calibrate Roots meters, which are positive displacement meters.

Displacement Bottle Technique - Primary Standard

The displacement bottle consists of a bottle filled with water (or some other liquid) and a tube through which air can enter the bottle (Figure 3-19). As the liquid in the bottle is drained or siphoned out, air is drawn in to take the place of the volume of liquid lost. The volume of gas sampled is equal to the volume of liquid displaced.

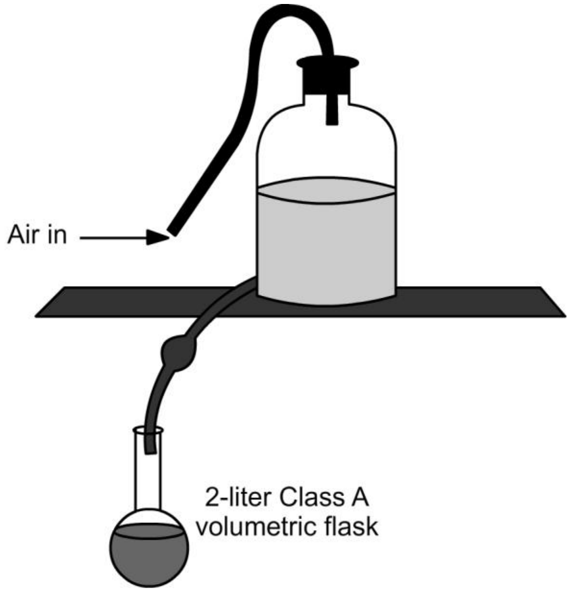

Figure 3-19. Displacement bottle technique.

The fluid in the displacement bottle should be in thermal equilibrium with the room temperature. This equilibrium will ensure no liquid evaporation from the bottle water to the air, and will simplify volume corrections for *T* and *P*. The volume of displaced liquid can be measured with a graduated cylinder or Class A volumetric flask, depending on how accurately the volume needs to be measured. Accuracy can range from 1 to 5%, depending on what measuring device is used. A NIST-traceable volumetric flask (e.g., Class A designation) must be used for this method to be considered as a primary standard. The displacement bottle as used in this technique simply serves as the air mover.

Again, once the volume of air has been determined at room conditions, it should be converted to the volume at standard conditions. This conversion uses the relationship previously stated in Equation 3-10.

Frictionless Pistons - Primary Standard

The soap-bubble meter and the mercury-sealed piston are two frictionless pistons. Mercury-sealed piston meters are no longer available; however, some remain in use. Accurate and convenient measurement of flows between 1 and 1000 mL/min can be made with a soap-bubble meter. Some mercury-sealed pistons can accurately measure flows from 100 cm^3/min to 24,000 cm^3/min.

Moving-Bubble Meter

A bubble meter consists simply of a cylindrical glass tube with graduated markings, usually in milliliters. Inverted burets are often used as soap-bubble meters (Figure 3-20); however, burets cannot be used with anything other than a vacuum source. Simple bubble meters (Figure 3-21) can be purchased, although the basic design can be made conveniently by a competent glass blower.

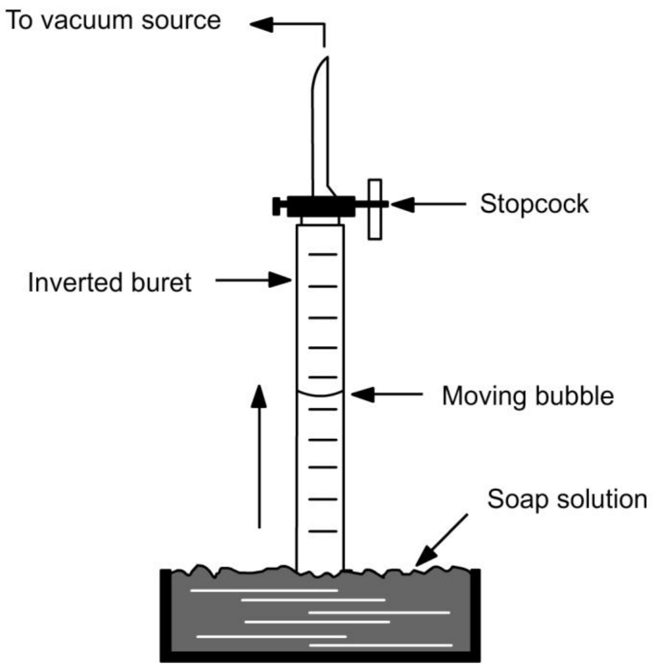

Figure 3-20. Moving-bubble meter.

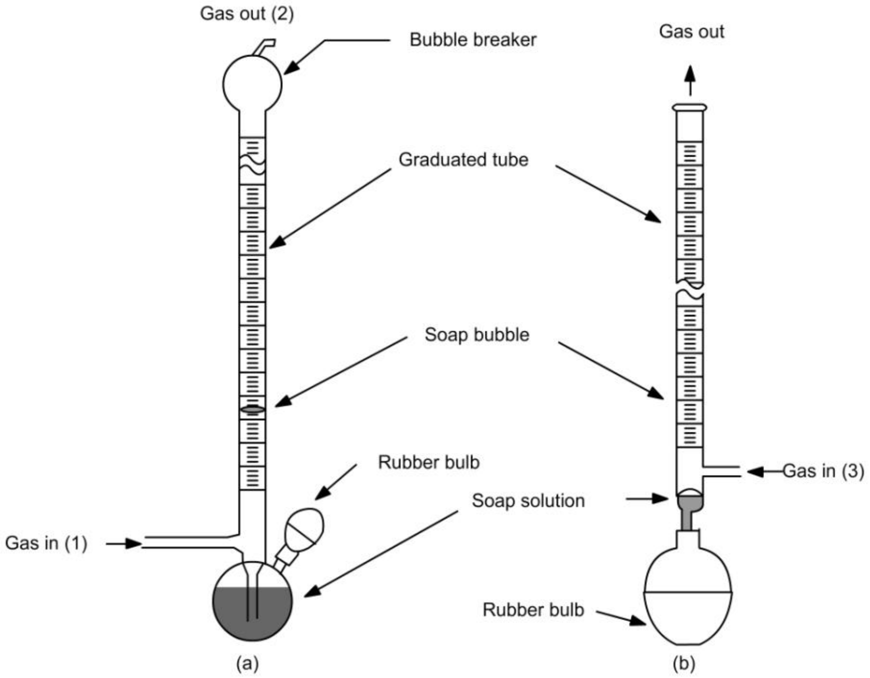

Figure 3-21. Moving-bubble meters: (a) one with bubble breaker and capability of handling vacuum at (2) or pressure at (1); (b) one capable of handling only pressure at (3).

The moving-bubble meter is one of the simplest of primary standards. The inside walls of the tube are wetted with a soap solution. A bubble is formed by touching the tip of the buret to the soap solution, as in Figure 3-20, or by squeezing the rubber bulb until the soap solution is raised above the gas inlet (Figure 3-21).

Either a vacuum at the top or slight positive pressure at the bottom of the tube moves the bubble (a frictionless piston) up the tube. By timing this movement and noting the volume traversed by the bubble over the measured time span, volumetric flow rate can be calculated.

The volume measured by a moving-bubble meter must be corrected for two conditions. First, if the room temperature and pressure are different from standard atmospheric conditions, the volume must be corrected by the relationship previously stated (Equation 3-10):

(Eq. 3-11)

$$V_2 = V_1\left(\frac{P_1}{760\,\text{mm Hg}}\right)\left(\frac{298\text{K}}{T_1}\right)$$

Where:

V_2 = *volume of gas at* 2^{nd} *conditions or at* P_2 *and* T_2
V_1 = *a volume of gas at* 1^{st} *conditions of* P_1 *and* T_1
T_1 = *initial temperature of gas, K*
T_2 = *final temperature of gas (in this case, 298 K)*
P_1 = *initial pressure of gas, mm Hg*
P_2 = *final pressure of gas (in this case, 760 mm Hg)*

Second, the measured volume can be slightly larger than the standardized volume because water from the bubble evaporates into the gas behind the bubble. If the gas behind the bubble has a relative humidity greater than 50%, the error is small. If the gas is dry, the error can be large and must be corrected by the following formula:

(Eq. 3-12)

$$V_c = V_{meas}\left(\frac{P_b - P_w}{P_b}\right)$$

Where:

V_c = *corrected volume*
V_{meas} = *measured volume*
P_b = *atmospheric pressure, mm Hg*
P_w = *vapor pressure of water at the room temperature, mm Hg.*

Note that P_b and P_W must have the same units (Torr and mm Hg are equivalent).

Table 3-1. Vapor pressure table.[1]

TEMPERATURE (C°)	VAPOR PRESSURE (TORR)
15° C	12.8
16° C	13.6
17° C	14.5
18° C	15.5
19° C	16.5
20° C	17.6
21° C	18.7
22° C	19.8
23° C	21.1
24° C	22.4
25° C	23.8
26° C	25.2
27° C	26.8
28° C	28.4
29° C	30.1
30° C	31.9

Moving-bubble meters can be calibrated by measuring the dimensions of the tube; however, poor control on glass dimensions in manufacturing make this inaccurate. The bubble meter is usually calibrated by filling the tube with a liquid (water or mercury, for example), then draining the liquid from the top graduation to the bottom graduation. The volume or weight of the collected liquid can be measured. Since water is susceptible to thermal expansion and contraction, proper corrections for temperature must be made if this calibration is to be accurate. The moving-bubble meter should only be used to measure volumes between graduations that have been calibrated.

The bubble meter is used almost exclusively in laboratory situations for calibration of other air-measuring instruments. In average laboratory conditions, the moving-bubble meter is accurate to about ± 1%, depending on how accurately it is calibrated. Accuracy decreases for flows below 1 mL/min and above 1 L/min mainly because of gas permeation through the bubble. A detailed description of the calibration and use of bubble meters has been published by Levy (1964). Increased accuracies have been reported for bubble meters fitted with automatic sensing devices that start and stop a timer.

Mercury-Sealed Piston

An electronically-actuated mercury-sealed piston is no longer commercially available and is rarely encountered today due to the health and environmental

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[1] A more detailed saturation water vapor table can be found in the appendix.

issues associated with mercury. In its day, the mercury-sealed piston was considered expensive; however, its accuracy (± 0.2% for time intervals greater than 30 seconds) and simple operation make it an extremely useful tool.

The mercury-sealed piston consists of a precision-bored, borosilicate glass cylinder with a close-fitting polyvinyl chloride piston (Figure 3-22). The piston and cylinder wall are sealed with a ring of mercury that stays in place because of its high viscosity and the closeness of the fit between the cylinder and piston. Gas entering the solenoid valve is vented until the measurement cycle is actuated. When the measurement cycle is started, the solenoid valve closes the vent, allowing gas to enter the cylinder.

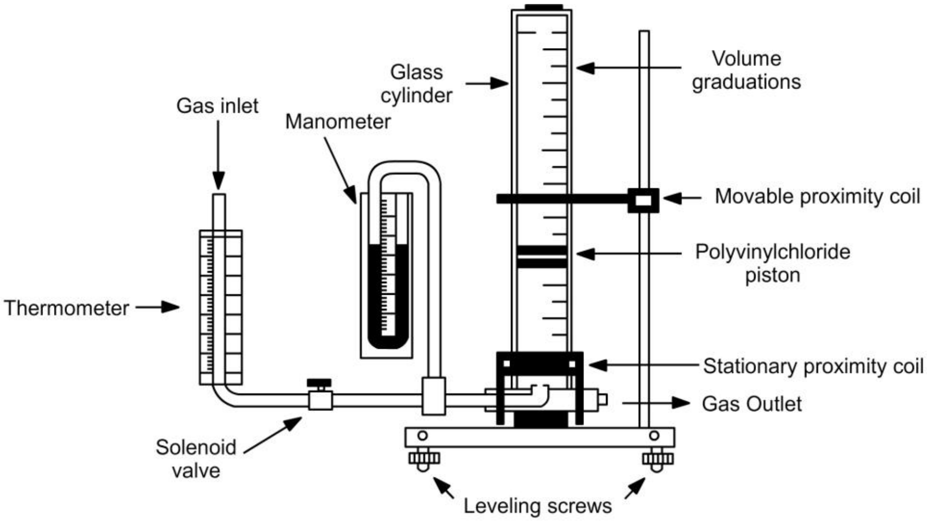


Figure 3-22. Mercury-sealed piston volume meter.

A timer is started and stopped as the mercury seal passes the lower and upper proximity coils (metal detectors). The volume displaced can be set by adjusting the upper proximity coil. The volume is corrected to standard conditions using the pressure drop across the piston (usually < 3 inches of water). The measured time and the corrected volume can be used to calculate volumetric flow.

Calibration of the mercury-sealed piston volume meter is usually performed by the manufacturer. The borosilicate glass cylinder is bored to a precise diameter. The inside diameter is air-gauged at least every inch to check for consistency. Before the instrument is sent out it is compared to a standard-mercury-sealed piston volume meter that is traceable to NIST.

Although mercury-sealed piston meters are no longer available, similar devices such as automated soap-bubble meters and automated non-mercury based piston meters (i.e. dry-piston meters) are commercially available and in widespread use today.

Automated Bubble Flowmeters

A semiautomatic bubble flowmeter instrument is easier to use than the manual version and is likely to provide more uniform and accurate flow rate measurements, particularly at relatively high flow rates. An electronic "eye" records time, *zero*, when the soap bubble passes an initial point, while a second electronic eye, representing a set volume relative to the initial point, records time, *t*. The elapsed time divided into the known volume the soap-bubble traversed between the electronic eyes provides the flow rate. The instrument's digital readout is typically in units of liters per minute. Automated bubble flowmeter kits, such as the Gilibrator, are equipped with 3 cells that allow for flow measurements of a few milliliters per minute to up 30 liters per minute.

Because the liquid used to form the bubbles is usually water-based, a water vapor correction may be required to compensate for a volume increase due to evaporation of the water in the instrument, as discussed in the moving-bubble meter section above. Furthermore, the instrument cannot be used below 0°C because the soap solution will freeze. It is also susceptible to persistent drying of the cell wall and temperature variations when exposed to direct sunlight, which results in diminished accuracy.

Automated Dry-Piston Flowmeters

Dry-piston flowmeters are similar to soap-bubble flowmeters except they use a lightweight, low-friction, rigid piston in place of the soap-bubble. These flowmeters are relatively easy to use and are not subject to the water vapor correction of the liquid-freezing limitation of the bubble flowmeters or the dry influence of sunlight when used in the field. However, they may still be subject to a lower operational temperature limit due to LCD readouts.

Wet Test Meter (WTM) - Secondary Standard

The wet test meter consists of a series of inverted buckets or traps mounted radially around a shaft and partially immersed in water (Figure 3-23a). The location of the entry and exit gas ports is such that the entering gas fills a bucket, displacing the water and causing the shaft to rotate due to the lifting action of the bucket full of air. The entrapped air is released at the upper portion of the rotation and the bucket again fills with water. In turning, the drum rotates index pointers that register the volume of gas passed through the meter (Figure 3-23b).

After the meter is leveled, the proper water level is achieved by using the filling funnel, fill cock, and drain cock (Figure 3-23c) to bring the meniscus of the water in touch with the tip of the calibration index point. The calibration gas should be passed through the meter for one hour to saturate the water with the gas. The water in the meter should be at the same temperature as the surrounding atmosphere, to avoid the need to make a correction for temperature. If any water is added, sufficient time must be allowed for complete equilibration.

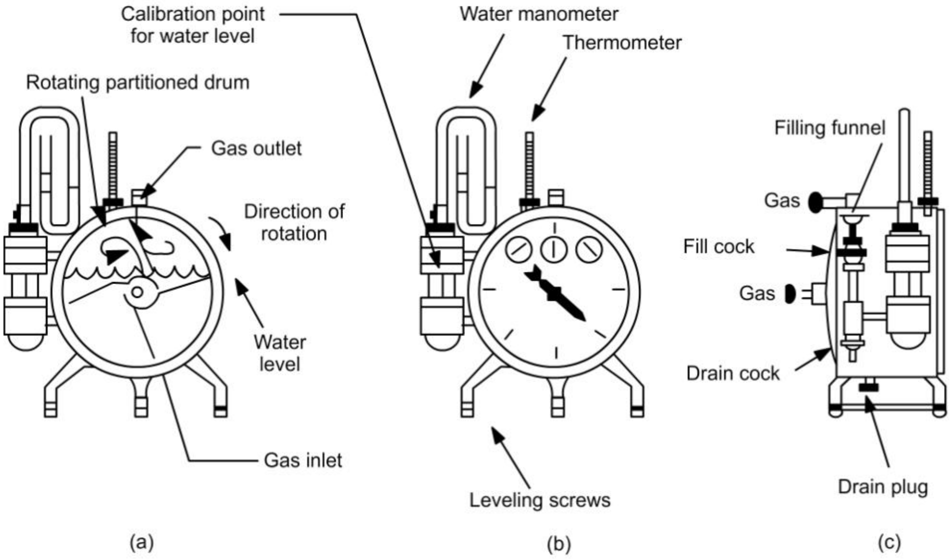


Figure 3-23. Wet test meter.

Once the water level is set and the meter is equilibrated, the wet test meter is ready for calibration (or for use if it is already calibrated). An accurate calibration of a wet test meter can be done with a spirometer (Figure 3-24).

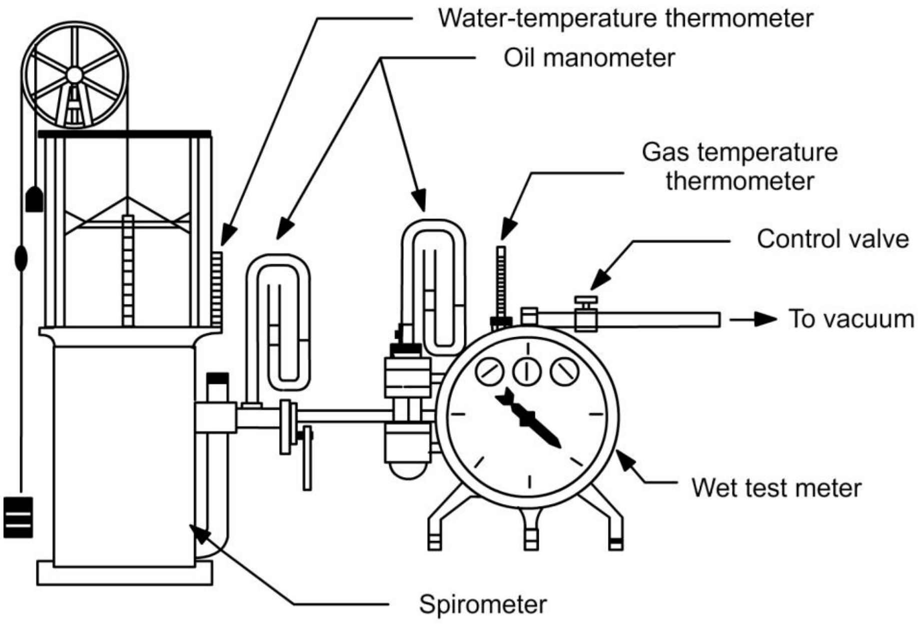


Figure 3-24. Setup for calibrating a wet test meter against a spirometer.

The wet test meter can also be calibrated against a bubble flowmeter or dry-piston meter.

Enough gas is drawn through either system to turn the wet test meter at least three revolutions and to significantly move the spirometer drum, soap bubble, or piston. The measurement is made several times. Atmospheric pressure and temperature, and the temperature and pressure differential for both the wet test meter and calibrating device, are needed to correct the volume to standard conditions (taking pressure differentials, as indicated by the oil manometers, into consideration). Since both the calibration device and the wet test meter are measuring a dry gas stream, a significant error is introduced if the measured volume is not corrected to dry conditions. This correction is the same as for the soap-bubble meter correction:

(Eq. 3-13)

$$V_c = V_{meas}\left(\frac{P_b - P_w}{P_b}\right)$$

Where:

V_c = *corrected volume* (V_2)
V_{meas} = *measured volume* (V_1)
P_b = *atmospheric pressure, mm Hg*
P_w = *vapor pressure of water at the room temperature, mm Hg*

A simple calibration check can be performed using a displacement bottle, as shown in Figure 3-25. After all the water is thermally equilibrated, the wet test meter is properly set up, the drain tube of the displacement bottle is filled, and the pinch clamp is opened, allowing 2 liters of water to drain into a 2-liter Class A volumetric flask. The corresponding wet test meter readings are taken. This is repeated several times (usually four).

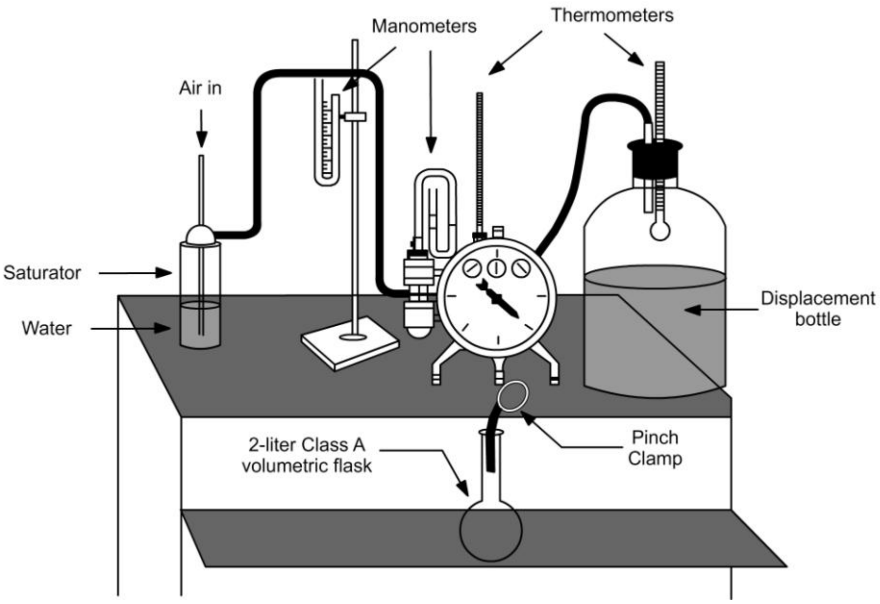


Figure 3-25. Calibration of wet test meter with displacement bottle.

The calibration data can be used to:

1. Draw a multipoint calibration curve.
2. Adjust the calibration index point so that the meter volume is correct.
3. Calculate a correction factor for the wet test meter.

Wet test meters should check within ± 0.5 % if option 2 is used. All volumes measured by a wet test meter should be corrected to standard conditions by Equation 3-10.

Wet test meters are used as transfer standards because of their high accuracy (less than ± 1%). Because of their bulk, weight, and equilibration requirements, they are seldom used outside a laboratory setting. Wet test meters are useful for laboratories that need an accurate standard yet do not have the funds or space for a spirometer. Wet test meters can be used to measure flow rates up to 3 revolutions/min, at which point the meter begins to act as a limiting orifice and obstructs the flow. Wet test meters are available in sizes that correspond to 1, 3, and 10 L/rev.

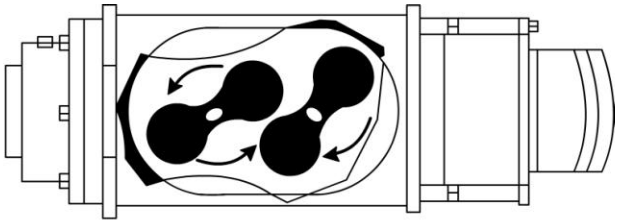
Roots Meter - Secondary Standard

The Roots meter is a positive displacement, rotary-type meter for measuring volume flow. It is suitable for handling most types of clean, common gases. It is not suitable for handling liquids, and its operation can be impeded by excessive particulate matter carried in the gas stream.

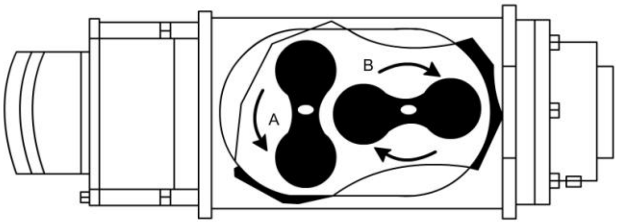
Roots meters consist basically of two oppositely rotating impellers of two-lobe or "figure eight" contour, operating within a rigid casing (Figure 3-26). The casing is arranged with inlet and outlet gas connections on opposite sides. Impeller contours are mathematically developed and accurately produced, and are of such form that a continuous seal without contact can be maintained between the impellers at all positions during rotation. To accomplish this, the correct relative impeller positions are established and maintained by precision-grade timing gears. Similar seals exist between the tips of the impeller lobes and the two semicircular parts of the meter casing. As a result of this design, the gas inlet side of the meter is always effectively isolated from the gas at the outlet side of the impellers. Consequently, the impellers can be caused to rotate by a very small pressure drop across the meter.

The rotation of the impellers is in the direction indicated in Figure 3-26, and as each impeller reaches a vertical portion (twice in each revolution), it traps a known specific volume of gas between itself and the adjacent semicircular portion of the meter casing at A and B (Figure 3-26, Position 2). Thus, in one complete revolution, the meter will measure and pass four similar gas volumes, and this total volume is the displacement of the meter per revolution.

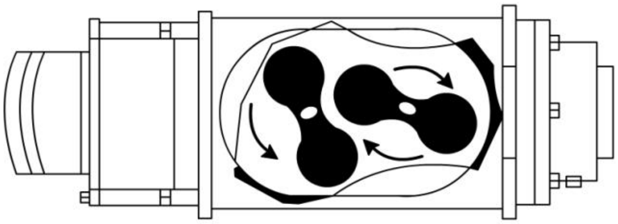
The displacement of volume of the Roots meter is precisely determined by the manufacturer, both by calculation and by testing it using a known volume of air or other gas. Roots meters are usually calibrated against large spirometers prior to shipment. Users do not usually have a way to calibrate Roots meters and must depend on the supplied calibration data. Volumetric accuracy of the Roots meter is permanent and nonadjustable (except for linkage adjustment), because its measuring characteristics are established by the dimensions and machined contours of nonwearing fixed and rotating parts.



Position 1



Position 2



Position 3

Figure 3-26. Principle of gas flow through the Roots meter.

The revolutions of the impellers are indexed with the meter reading calibrated in a volume unit (i.e., ft^3 or m^3). Units are sold that have temperature compensation devices, but corrections to standard temperature and pressure conditions are easily made with the previously mentioned formula given in Equation 3-10 (pressure drop across the Roots meters should be taken into consideration).

(Eq. 3-14)

$$V_2 = V_1\left(\frac{P_1}{760\,\text{mm Hg}}\right)\left(\frac{298\,\text{K}}{T_2}\right)$$

Where: V_2 = *volume of gas at* 2^{nd} *conditions or at* P_2 *and* T_2
V_1 = *a volume of gas at* 1^{st} *conditions of* P_1 *and* T_1
T_1 = *initial temperature of gas, K*
T_2 = *final temperature of gas (in this case, 298 K)*

P_1 = *initial pressure of gas, mm Hg*
P_2 = *final pressure of gas (in this case, 760 mm Hg)*

The symbol P_1, in this instance, is the atmospheric room pressure (P_b, in mm Hg) minus the pressure drop across the Roots meter Δp , in mm Hg.

(Eq. 3-15) $$P_1 = P_b - \Delta p$$

The metering unit is magnetically coupled to the impellers. The entire counting unit is enclosed in a plastic cover. The cover also holds oil that lubricates the metering device. The proper oil level is set by the inscribed oil level lines on the ends of the plastic covers. The user of a Roots meter must be careful not to severely tilt the meter when oil is in the plastic cover, as this can force oil into the impeller casing. If the oil gets into the impeller casing, flushing with kerosene can remove the oil.

Although Roots meters are widely used in industrial applications, they have been used almost exclusively as the standard for high-volume sampler flow rate in atmospheric sampling applications.

Dry Test Meter - Secondary Standard

Dry *test* meters are an improvement over the more common dry *gas* meters (Figure 3-27). Dry gas meters (a secondary standard) are most commonly used in residential and industrial settings to measure gas flow (e.g., natural gas). The dry test meter (a secondary standard) works on the same principle as the dry gas meter (a secondary standard), but a different indexing method (read-out) makes it more accurate (usually ± 1 to 2% when new). The dry test meter shown in Figure 3-28 shows the new read-out mechanism.

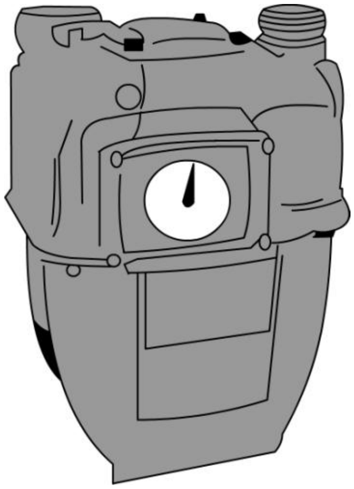


Figure 3-27. Dry gas meter.

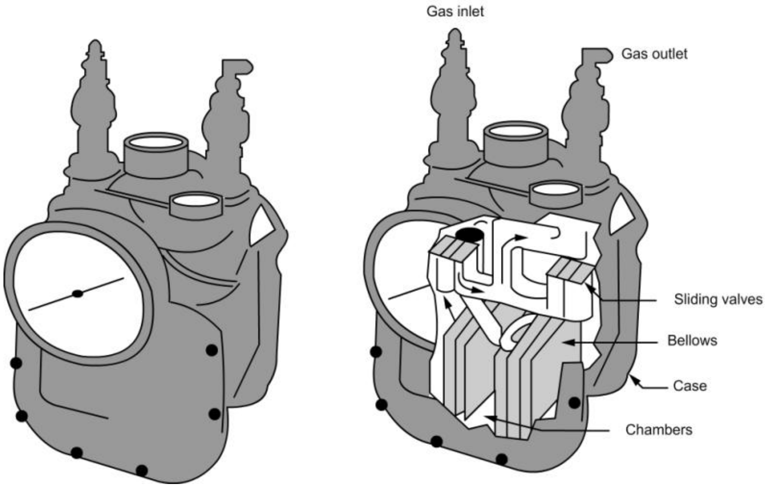


Figure 3-28. Dry test meter.

The interior of the dry test meter contains two or more movable partitions, or diaphragms, attached to the case by a flexible material so that each partition may have a reciprocating motion (Figure 3-29). The gas flow alternately inflates and deflates each bellows chamber, simultaneously actuating a set of slide valves that shunt the incoming flow at the end of each stroke. The inflation of the successive chambers also actuates, through a crank, a set of dials that register the volume of gas passed through the meter.

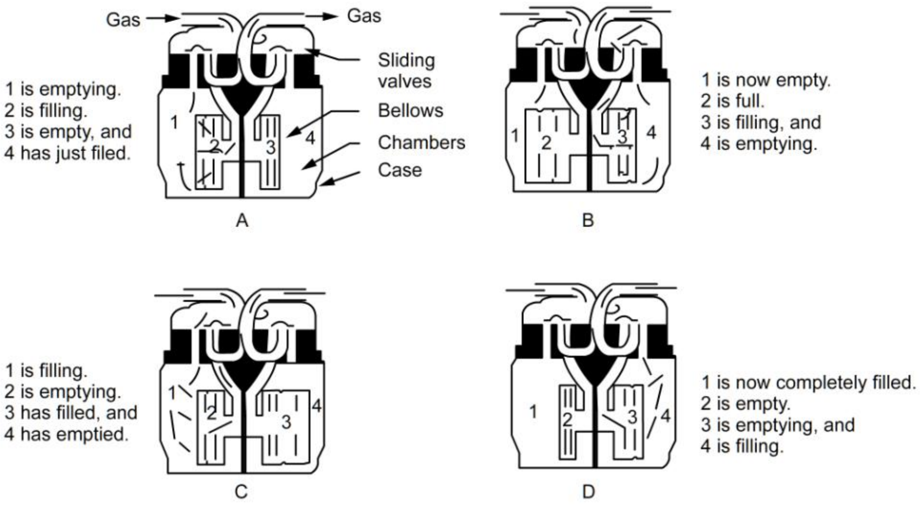


Figure 3-29. Working mechanism of dry test meter.

The dry test meter is calibrated against a spirometer, bubble flowmeter, piston flowmeter, or displacement bottle similar to the wet test meter. One big advantage of the dry test meter over the wet test meter is that no correction for water vapor is needed. If the dry test meter is off calibration by more than 2%, it can be corrected by adjustment of the meter linkage. If linkage adjustment cannot correct the problem, then the dry test meter must be returned to the manufacturer for repairs.

Dry test meters are used in the field as well as in laboratory calibrations. Since the dry test meter does not contain water, it is lighter and easier to use than the wet test meter. Also, the dry test meter is more rugged than the wet test meter. Accuracy of the dry test meter does, however, worsen with age.

3.11 Rate Meters

Rate meters measure, indirectly, the time rate of the fluid flow through them. Their response depends on some property of the fluid related to the time rate of the flow.

Variable-Pressure Meters - Head Meters

Head meters are those in which the stream of fluid creates a significant pressure difference that can be measured and correlated with the time rate of flow. The pressure difference is produced by a constriction in the stream of flow causing local increase in velocity.

Orifice Meter – Noncritical – Secondary Standard

An orifice meter can consist of a thin plate having one circular hole coaxial with the pipe into which it is inserted (Figure 3-30). Two pressure taps, one upstream and one downstream of the orifice, serve as a means of measuring the pressure drop, which can be correlated to the time rate of flow. Watch jewels, small bore tubing, hypodermic needles, and specially manufactured plates or tubes with small holes have been used as orifice meters. The pressure drop across the orifice can be measured with a manometer, magnehelic, or pressure gauge.

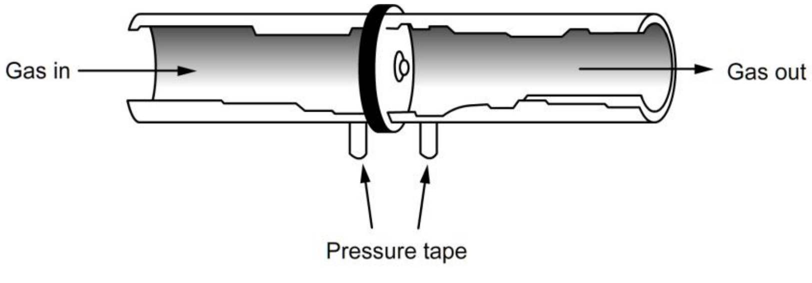


Figure 3-30. Orifice meter.

Flow rates for an orifice meter can be calculated using Poiseuille's Law; however, this is not done for practical use. Instead, the orifice meter is usually calibrated with either a wet or dry test meter, or a bubble meter. A typical calibration curve is shown in Figure 3-31.

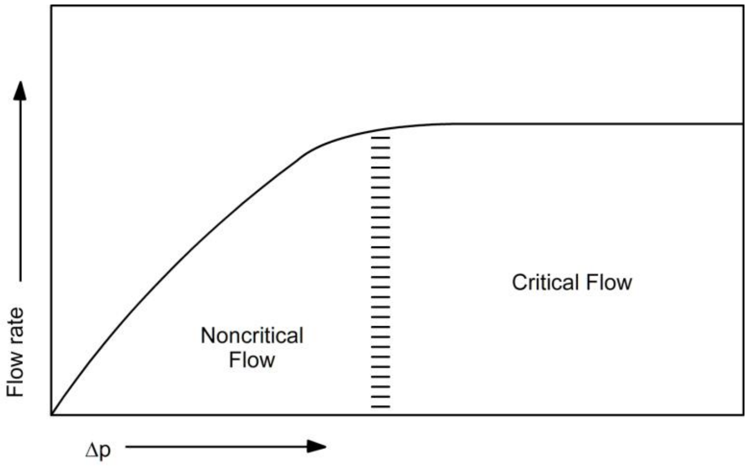


Figure 3-31. Typical orifice meter calibration curve.

Calibration curves for orifice meters are nonlinear in the upper and lower flow rate regions and are usually linear in the middle flow rate region.

Orifice meters can be made by laboratories with a minimum of equipment. They are used in many sampling trains to control the flow. However, since a non-critical orifice meter is operated in the noncritical (or subsonic, below the speed of sound) portion of the curve (Figure 3-31), change in flow occurs as a result of variations in pressure. The change in pressure over the orifice meter may be from an alteration to the driving force of the air mover (e.g., pump) or as a result of a "filter cake" building up on a filter, creating increased resistance in the sampling train, as more and more particles are captured. A sampling train which utilizes an orifice meter must be properly designed and operated to ensure a known volume of gas is sampled and the collection device is operated at its design flow rate.

Care must be exercised to avoid plugging the orifice with particles. A filter placed upstream of the orifice can eliminate this problem. Orifice meters have long been used to measure and control flows from a few mL/min to 50 L/min.

Orifice Meter – Critical – Secondary Standard

If the pressure drop across the orifice (Figure 3-30) is increased until the downstream pressure on an absolute basis is equal to approximately 0.53 times the upstream pressure on an absolute basis (for air and some other gases), the velocity of the gas in the constriction will become acoustic, or sonic. Orifices used in this manner are called critical orifices. The constant 0.53 is purely a theoretical value and may vary. Any further decrease in the downstream pressure or increase in the upstream pressure will not affect the rate of flow. As long as the 0.53 pressure relationship exists, the flow rate remains constant for a given upstream pressure and temperature, regardless of the value of the pressure drop (Figure 3-31). The error of an orifice meter is approximately 2%.

Only one calibration point is needed for a critical orifice. The critical flow is usually measured with a moving-bubble meter, or a wet or dry test meter. Corrections for temperature and pressure differences in calibration and use are made with the following formula:

(Eq. 3-16)

$$Q_2 = Q_1\left(\frac{P_1 \times T_2}{P_2 \times T_1}\right)$$

Where:

Q = *flow*
P = *pressure*
T = *temperature in K*
1 = *initial conditions*
2 = *final conditions*

The same formula can be used to correct orifice meter flows to standard conditions by substituting P_2 = 760 mm Hg and T_2 = 298 K. Note the square root function of T and P. *Any time that rate meters are corrected for* T *and* P_1 *this square root function is needed.*

Critical orifices are used in the same types of situations as noncritical orifices and many of the same design and operational considerations apply. However, since critical orifice meters operate in the critical (or supersonic, above the speed of sound) portion of the curve (Figure 3-31), flow does not change unless the relative variation in pressure falls below the ratio of 0.53 ($P_{downstream}$ / $P_{upstream}$). In other words, even as a filter cake builds, as long as the air mover (e.g., pump) has sufficient capacity, flow is unaffected until the ratio of the pressures across the orifice meter falls below the theoretical value of 0.53. Care must also be taken not to plug the orifice.

Critical orifice meters are often used when sampling with an evacuated flask. A critical orifice at the inlet of the flask maintains a constant flow rate over a known period of time.

Venturi Meter - Secondary Standard

The venturi meter consists of a short cylindrical inlet, an entrance cone, a short cylindrical throat, and finally a diffuser cone (Figure 3-32). Two pressure taps, one in the cylindrical inlet and one in the throat, serve to measure the pressure drop. There is no abrupt change of cross section as with an orifice; thus the flow is guided both upstream and downstream, eliminating turbulence and reducing energy losses. Venturi meters are, of course, more difficult to fabricate. The probable error of a venturi is 1%.

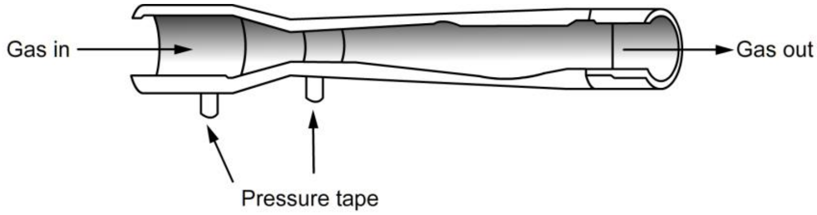


Figure 3-32. Venturi meter.

The venturi meter is calibrated in the same manner as the orifice meter. The calibration curve generated plots pressure drop across the venturi versus flow rates determined by the standard meter. Venturi meters are always used in the noncritical flow region and are therefore analogous to a noncritical orifice meter; however, they are typically designed to operate at much higher flow rates than the orifice meter. Venturi meters are generally used to calibrate the rotameter (i.e. visi-float) integral to a "Hi-Vol" vacuum cleaner-type pump used in high volume sampling.

Variable Area Meters

The variable area meter differs from the fixed orifice; the pressure drop across it remains constant while the cross-sectional area of the constriction (annulus) changes with the rate of flow. A rotameter is an example of a variable area meter.

Rotameter – Secondary Standard

The rotameter consists of a vertically graduated glass tube, slightly tapered in bore with the diameter decreasing from top to bottom, containing a float of the appropriate material and shape (Figure 3-33). The fluid to be measured passes upward through the conical tube, which is inserted in the flow circuit.

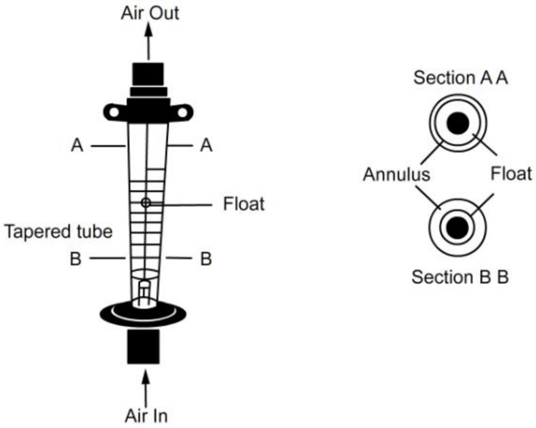


Figure 3-33. Rotameter.

A specially-shaped float, with a diameter slightly greater than the minimum bore of the conical tube, is carried upward by the passage of the fluid until it reaches a position in the tube where its weight is balanced by the upward forces due to the fluid flowing past it. A variable ring or annulus is created between the outer diameter of the float and the inner wall of the tube. As the float moves upward in the tube, the area of the annulus increases (Figure 3-33, Sections AA and BB). The float will continue to move upward until a pressure drop across the float, which is unique for each rotameter, is reached. This pressure drop across the float is constant regardless of the flow rate. A measure of the flow is noted by the float position on a vertical scale and compared with a calibration chart to determine the corresponding flow rate in units such as mL/min or L/min.

The flow rate through a rotameter can be calculated from the tube diameters, float dimensions, float composition, and gas characteristics; this is not commonly done for calibration purposes. A detailed development of the flow equations for rotameters is contained in the appendix of this manual. Manufacturers generally provide accurate calibration curves for rotameters; it is advisable, however, to calibrate a rotameter under its operating conditions (i.e., connected to the other components of the sampling train as it will be used).

Most rotameters are used and calibrated at room temperature with the downstream side at atmospheric pressure. Corrections for pressure and temperature variations can be made using the previously mentioned formula:

(Eq. 3-17)

$$Q_2 = Q_1\left(\frac{P_1 \times T_2}{P_2 \times T_1}\right)$$

Where:
Q = *flow*
P = *pressure*
T = *temperature in K*
1 = *initial conditions*
2 = *final conditions*

If a gas is measured with a different density from the calibration gas, the flow rate can be corrected using the following formula:

(Eq. 3-18)

$$Q_1 = Q_2\left(\frac{q_2}{q_1}\right)^{1/2}$$

Where:
Q_1 = *flow rate with gas 1*
Q_2 = *flow rate with gas 2*
q_2 = *density of gas 2*
q_1 = *density of gas 1*

Because corrections of this type are cumbersome and add inaccuracies, rotameters are usually calibrated under normal operating conditions against a primary standard.

Rotameters are the most widely used laboratory and field method for measuring gas or liquid flow. Their ease of use makes them excellent for spot flow checks. With proper calibration, the rotameter's probable error is 2 to 5%. In the past, many atmospheric sampling instruments used rotameters to indicate the sample flow rate. Today, they have been, to a great extent, replaced by mass flow meters and/or mass flow controllers.

Mass Flow Meters – Heat Transfer Meters – "Hot-Wire" Meters

Mass flow meters (MFMs) operate on the principle that when a gas passes over a heated surface, heat is transferred from the surface to the gas. For gases that approximate the behavior of ideal gases, the quantity of heat transferred and the resulting temperature differential is proportional to the mass (or weight) of the gas. The mass flow of the gas, as measured by the meter, is also directly proportional to volumetric flow rate.

There are two basic applications of the principle of mass flow to atmospheric sampling and monitoring instrumentation: mass flow meters (measures volumetric flow rate) and mass flow controllers (measures and controls volumetric flow rate).

Mass Flow Meter – Secondary Velocity Standard

A mass flow meter (MFM) consists of a transducer and separate power supply and electronic digital readout. The sample gas passes through the transducer, which contains a heated surface (e.g., wire, coil-wire metallic block combination) that transfers heat to the sample gas; heat is transferred from this surface to the gas. The amount of current required to keep the surface at a constant temperature is proportional to the mass and velocity of the gas, which is in turn proportional to the volumetric flow rate. The MFM provides a digital readout in volumetric flow rate units such as SLPM, SCCM, or SCFM.

Atmospheric sampling applications of the MFM are usually limited to the measurement of volumetric flow. Since these devices measure mass flow directly, they should be calibrated against a primary or secondary volumetric standard. The standard flow meter is corrected to standard conditions (STP) and compared to the mass flow rate measured by the MFM.

No corrections for temperature and pressure need to be made to the mass flow meter readings since the principle of measurement is mass flow, which is not influenced by changes in temperature and pressure. However, mass flow meters are designed based on a particular standard temperature and pressure. It may have been designed and initially calibrated at the same standard temperature and pressure typically used in atmospheric sampling and ambient monitoring (298 K, 760 mm Hg), or it may have been performed at other conditions (e.g., 273 K, 760 mm Hg). If the latter is true, a correction to the flow rate, as measured by the MFM, should be performed using Equation 3-16.

Calibration must be done with the same gas as will be measured in use, because different gases have different thermal properties. If the sample gas differs from the manufacturer design and calibration gas for a particular MFM (typically N_2), the flow rate as measured by the MFM should be corrected by applying a gas correction factor (GCF). The GCF can be determined experimentally by passing the sample gas through a standard flow meter (e.g., automated bubble meter) and the MFM to determine the difference in volumetric flow. Alternatively, a GCF can be calculated based on the ratio of the molar specific heat for the standard gas and the sample gas, using Equation 3-18.

(Eq. 3-18)

$$GCF = \frac{C_{pN_2}}{C_{pgasx}}$$

Where:

GCF = *gas correction factor*

C_{pN_2} = *molar specific heat for* N_2 *gas (the typical gas used to calibrate a MFM)*

C_{pgasx} = *molar specific heat for the sample gas*

The more accurate published molar specific heat data is determined empirically by investigators. These data (i.e., C_p) can be found in the literature or from the National Institute of Standards and Technology (NIST).

The accuracy of a MFM is typically +/- 1-2% of full scale and is most often used for flow measurement or as calibration transfer devices in the field and laboratory. Their insensitivity to temperature and pressure makes them a useful tool for standard conditions measurement.

It is advisable not to use a MFM in applications where corrosive and/or explosive gases are present. Another potential limitation is in applications whether the relatively large pressure drop associated with most MFMs is problematic (e.g., pump capacity too low). Manufacturers have designed a low pressure drop MFM to accommodate applications where pressure drop is critical.

Mass Flow Controller – Secondary Standard

The principle of operation for a mass flow controller (MFC) is the same as for the mass flow meter (MFM). The MFC has a very useful feature in addition to measuring the volumetric flow rate; it is capable of controlling the flow at a user-selected rate within the range of the instrument. This is accomplished with an electronic solenoid within the transducer which opens or closes to control the flow. This unique feature makes MFCs particularly useful in dynamic calibration devices. Dynamic calibrators are used to blend gases at precise flow rates to generate a known concentration used to calibrate automated air samplers and monitors. The disadvantages associated with a MFC are identical to those of a MFM.

3.12 Velocity Meters

Velocity meters measure the linear velocity or some property that is proportional to the velocity of a gas. Several instruments exist for measuring the velocity of a gas; we will discuss only the pitot tube and the thermal anemometer. Volumetric flow information can be obtained from velocity data, if the cross-sectional area of the duct is known, using the following formula:

(Eq. 3-19) $$Q = A\bar{v}$$

Where:

Q = volumetric flow rate, m^3/min

$\bar{v}$ = average velocity, m/min

A = cross sectional area, m^2

Pitot Tube – Primary Velocity Standard

The pitot tube is a simple pressure-sensing device used to measure the velocity of fluid flowing in an open channel. The complexity of the underlying fluid-flow principles involved in a pitot tube gas-velocity measurement is not apparent in the simple operation of this device. The pitot tube should, however, be considered and treated as a sophisticated instrument.

The pitot tube actually measures the velocity pressure (Δp) of a gas stream. Gas streamlines approaching a round object placed in a duct flow around the object, except at point "P_+," where the gas stagnates and the stagnation pressure (P_+) is found (Figure 3-34 and Figure 3-35a).

The static pressure in a gas stream is defined as the pressure that would be indicated by a pressure gauge if it were moving along with the stream so as to be at rest, or relatively "static," with respect to the fluid. The static pressure can be measured as shown in Figure 3-35b.

The difference between the stagnation pressure (P_+) and the static pressure (P_z) is the velocity pressure differential (Δp). This is shown in Figure 3-35c.

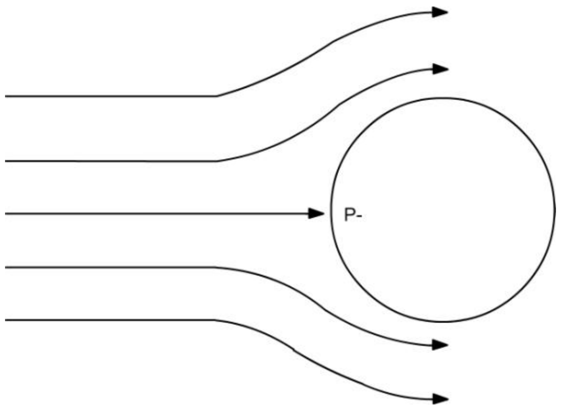


Figure 3-34. Gas stagnation against an object.

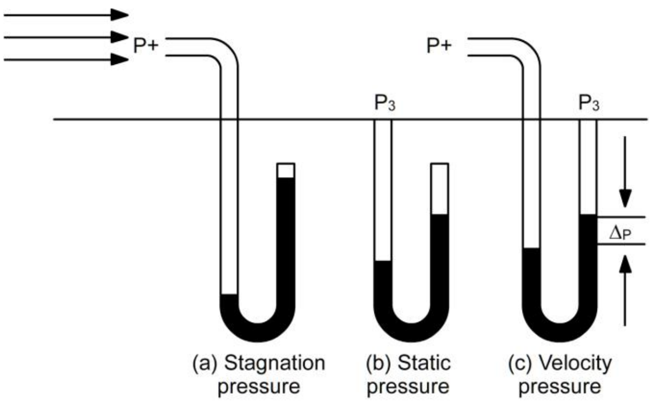


Figure 3-35. Pitot tube pressure components.

Bernoulli's Theorem relates pitot tube velocity pressure (Δp) to gas velocity in the following equation:

(Eq. 3-20)

$$v = K_p C_p \left(\frac{T \Delta p}{P\,M} \right)^{\frac{1}{2}}$$

Where:

v = *velocity of the gas stream, ft/sec*

T = *absolute temperature,* R *(°F+460)*

P = *absolute pressure, in. Hg*

M = *molecular weight of the gas, lb/lb-mole*

Δp = *velocity pressure, in.* H_2O

$$K_p = 85.49\ ft/\sec \sqrt{\frac{(lb/lb \bullet mole)(in.\,Hg)}{(in.\,H_2O)(°\mathrm{R})}}$$

C_p = *pitot tube coefficient, dimensionless.*

Pitot tubes are used extensively in ventilation work to measure air flow in ducts. Literature sources describe pitot tubes in detail. The standard and S-type pitot tubes are the most commonly used.

Standard Pitot Tube – Secondary Velocity Standard

The standard pitot tube (Figure 3-36) consists of two concentric tubes. The center tube measures the stagnation or impact pressure, and the static pressure is measured by the holes located on the side of the outer tube. The pitot tube must be placed in the flowing air stream so that it is parallel with the streamlines. The velocity pressure differential (Δp) can be measured with a U-tube manometer, inclined manometer, or any suitable pressure-sensing device. Only velocities greater than 2500 ft/min can be measured with a U-tube manometer, but flows as low as 600 ft/min can be measured with a carefully adjusted inclined manometer. Standard pitot tube velocity pressures are typically 0.14 inches of water at 1500 ft/min and 0.56 inches of water at 3000 ft/min.

The standard pitot tube was first calibrated against an orifice meter using Bernoulli's Theorem. Repeated calibrations proved that different standard pitot tubes have the same characteristic flow calibration. If the static pressure holes are six outer-tube diameters from the hemispherical tip and eight outer-tube diameters from the bend (Figure 3-39), then the theoretical C_p value in the previously mentioned formula is 1.0. Velocity determinations are seldom needed in atmospheric sampling, but are very common in source sampling. It is common practice in source sampling applications to assign a C_p value of 0.99 for a standard pitot, since empirical data indicates a slight positive bias, and to use English units (e.g., feet per second, inches of Hg, degrees Rankine [R]) as shown in Equation 3-21.

(Eq. 3-21)

$$v = K_p C_p \left(\frac{T \Delta p}{P\,M} \right)^{1/2}$$

Where:

v = *velocity of the gas stream, ft/sec*
T = *absolute temperature,* R *(°F + 460)*
P = *absolute pressure, in. Hg*
M = *molecular weight of the gas, lb/lb-mole*
Δp = *velocity pressure, in.* H_2O

$$K_p = 85.49\ ft/\sec \sqrt{\frac{(lb/lb \bullet mole)(in.\,Hg)}{(in.\,H_2O)(°\mathrm{R})}}$$

C_p = *pitot tube coefficient, dimensionless*

Standard pitot tubes can be used to measure linear velocity in almost any situation except in particle-laden gas streams. The particulate matter will foul the carefully machined tip and orifices. The velocity of gas streams with high particulate matter concentrations can be measured better with an S-type pitot tube.

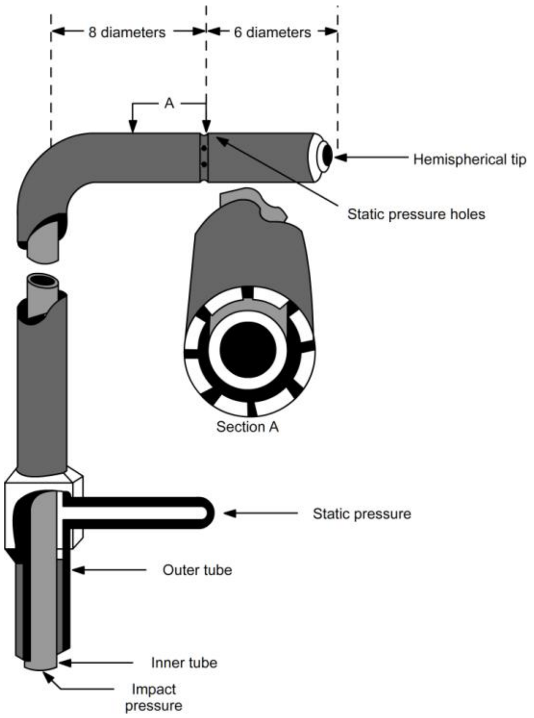


Figure 3-36. Standard pitot tube.

S-Type Pitot Tube – Secondary Velocity Standard

The S-type pitot tube consists of two identical tubes mounted back-to-back (Figure 3-37). The sampling ends of the tubes are oval with the openings parallel to each other. In use, one oval opening should point directly upstream, the other directly downstream. The tubes should be made of stainless steel or quartz if they are used in high temperature gas streams. The alignments shown in Figure 3-37 should be checked before use or calibration, as this may cause variations in the calibration coefficient (C_p).

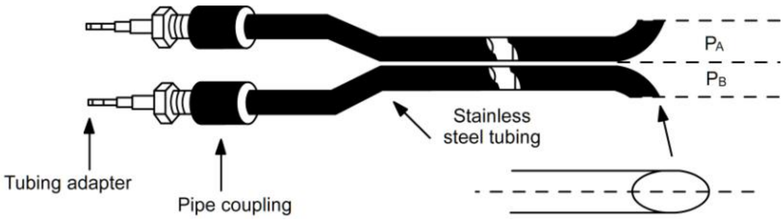


Figure 3-37. S-type pitot tube.

Calibration of the S-type pitot tube is performed by comparing it to a standard pitot tube. Both the standard and S-type pitot tubes are placed alternately into a constant air flow. Pressure readings are taken for the standard pitot tube and for leg A of the S-type tube, facing the direction of flow, and leg B, facing the direction of the flow (Figure 3-40). The pitot tube coefficient (C_p) is calculated using the following formula:

(Eq. 3-22)

$$C_{p(S)} = C_{p(STD)}\left(\frac{\Delta p_{STD}}{\Delta p_s}\right)$$

Where:
$C_{p(S)}$ = *S-Type Pilot tube coefficient*
$C_{p(STD)}$ = *Standard pitot tube coefficient*
Δp_{STD} = *velocity pressure of Standard pitot tube, in.* H_2O
Δp_s = *velocity pressure of S-Type pitot tube, in.* H_2O

The average C_p is calculated from several readings and should have a value of approximately 0.84. The C_p for leg A and leg B should differ by less than 0.01. The C_p value can then be used to calculate velocity by the previously mentioned formula.

(Eq. 3-23)

$$v = K_p C_p \left(\frac{T\Delta p}{P\,M}\right)^{1/2}$$

Where:
v = *velocity of the gas stream, ft/sec*
T = *absolute temperature,* R *(°F + 460)*
P = *absolute pressure, in. Hg*
M = *molecular weight of the gas, lb/lb-mole*
Δp = *velocity pressure, in.* H_2O
K_p = $85.49\ ft/sec\sqrt{\frac{(lb/lb \bullet mole)(in.\ Hg)}{(in.\ H_2O)(°R)}}$
C_p = *pitot tube coefficient, dimensionless*

The S-type pitot tube maintains calibration in abusive environments. The large sensing orifices minimize the chance of being plugged with particulates. The S-type pitot tube also gives a high manometer reading for a given gas velocity pressure, which can be helpful at low gas velocities. These features make the S-type pitot tube the most frequently used instrument to measure stack gas velocity.

Thermal Anemometer – Secondary Velocity Standard

A thermal anemometer measures fluid velocities by measuring heat transfer from a small wire or film held in the gas stream of a stack or duct or in the ambient air to measure wind speed. The rate by which heat is removed from the sensor is directly related to the velocity of the fluid flowing over the sensor. So, by measuring the amount of current required to maintain the sensor at a constant temperature, the fluid velocity can be obtained.

As suggested in the description of a thermal anemometer, these devices are typically used in source sampling applications to determine the velocity of a gas within a stack or duct. The use of a thermal anemometer in atmospheric sampling and monitoring is limited to wind speed determinations insofar as it influences sampling activities.

The advantages of thermal anemometry include high accuracy, an easily-automated collection procedure, and a high frequency response allowing measurement of turbulent flows.

3.13 Sample Problems

Problem 1: Volume Conversion to Standard Conditions

A volume of 20 m^3 was drawn from a spirometer at 20°C and 700 mm Hg. What was the standard volume drawn, based on EPA reference conditions for atmospheric sampling and monitoring?

$$V_2 = V_1\left(\frac{P_1 T_2}{P_2 T_1}\right)$$

Where:

V_2 = *volume at condition* 2

V_1 = *volume at condition* 1 = 20 m^3

P_1 = *pressure at condition* 1 = 700 mm Hg

P_2 = *pressure at condition* 2 = 760 mm Hg

T_1 = *temperature at condition* 1 = 20°C + 273 = 293K

T_2 = *temperature at condition* 2 = 25°C + 273 = 298K

$$V_2 = \left(20\text{m}^3\right)\left(\frac{700\,\text{mm Hg}}{760\,\text{mm Hg}}\right)\left(\frac{298\,\text{K}}{293\,\text{K}}\right)$$

$$V_2 = 18.7\ \text{m}^3$$

Problem 2: Orifice Conversion When Used at Other Calibration Conditions

An orifice was calibrated at 21°C and 760 mm Hg. It is to be used to calibrate a sampler at conditions of 25°C and 700 mm Hg. The flow at field conditions is 0.85 m^3/min (30 CFM). (a) What is the flow rate at calibration conditions? (b) What is the flow rate at standard conditions?

$$Q_2 = Q_1\left(\frac{T_2 P_1}{P_2 T_1}\right)^{1/2}$$

Where:

		Part a	*Part b:*
Q_2	= Flow 2	? (cal. condt.)	? (STD condt.)
Q_1	= Flow 1	0.85 m^3/min	Q_2 in Part a
P_2	= Press. 2	760 mm Hg	760 mm Hg
P_1	= Press. 1	700 mm Hg	700 mm Hg
T_2	= Temp. 2	21° + 273° = 294 K	298 K
T_1	= Temp. 1	25° + 273° = 298 K	294 K

(a) The flow rate at calibration conditions:

$$Q_2 = \left(0.85\,\mathrm{m^3/min}\right)\left(\frac{700\,\mathrm{mm\ Hg} \times 294\,\mathrm{K}}{760\,\mathrm{mm\ Hg} \times 298\,\mathrm{K}}\right)$$

$$Q_2 = 0.81\,\mathrm{m^3/min}$$

(b) The flow at standard conditions, using orifice data at calibration conditions and the flow derived in part (a):

$$Q_2 = Q_1\left(\frac{P_1 \times 298\,\mathrm{K}}{760\,\mathrm{mm\ Hg} \times T_1}\right)^{1/2}$$

$$Q_2 = 0.81\left(\frac{760\,\mathrm{mm\ Hg} \times 298\,\mathrm{K}}{760\,\mathrm{mm\ Hg} \times 294\,\mathrm{K}}\right)^{1/2}$$

$$Q = 0.82\,\mathrm{m^3/min}$$

Problem 3: Conversion for Different Gas Used with a Rotameter

A rotameter was calibrated with air at 0°C and 760 mm Hg. The rotameter is now to be used to add helium as a carrier gas at 0°C and 760 mm Hg. If the flow reading at point X on the rotameter corresponded to 28.3 liters/min (1 ft^3/min) when air is used, to what flow will point X correspond when helium is used? (Density of helium = 0.1785 g/L; density of air = 1.2929 g/L.)

$$Q_2 = Q_1\left(\frac{q_1}{q_2}\right)^{1/2}$$

Where:

Q_2 = *flow with gas* 2

Q_1 = *flow with gas* 1 = 28.3 L/min

q_1 = *density of gas* 1 = 1.2929 g/L *(air)*

q_2 = *density of gas* 2 = 0.1785 g/L *(helium)*

$$Q_2 = 28.3\left(\frac{1.2929\text{g/L}}{0.1785\text{g/L}}\right)^{1/2}$$

$$= 28.3(7.2431)^{1/2}$$

$$Q_2 = 76.2 \text{ L/min}$$

Problem 4: Pump Capacity

Can a pump with the following capacity curve (Figure 3-38) be used to drive critical orifices that have flow rates of (a) 50 cc/min and (b) 250 cc/min at criticality? (Hint: atmospheric pressure = 30 in. Hg.)

For an orifice to be critical,

$$P_{downstream} \leq 0.53 \text{ or} \leq 0.53(30) \text{ or} \leq 16 \text{ in. Hg.}$$

$$P_{downstream} = P_b + p_z \text{, therefore}$$

$$P_z = 30 - 16 = 14 \text{ in. Hg gauge vacuum}$$

At a gauge vacuum of 14 in. Hg, the pump can pull approximately 130 to 140 cc/min. Therefore, this pump could operate orifice (a) at 50 cc/min, but not (b) at 250 cc/min.

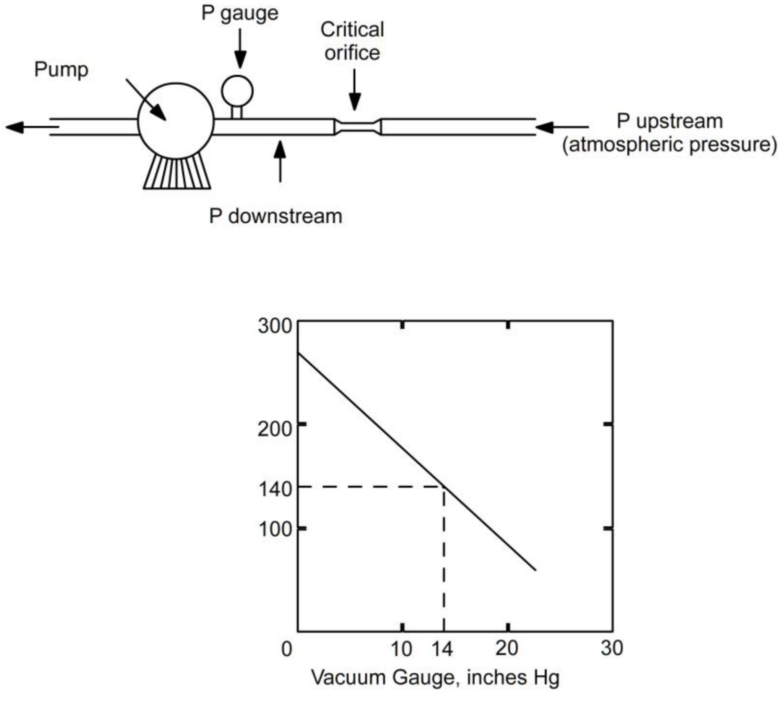


Figure 3-38. Problem 4: Pump capacity.

3.14 Additional $PM_{2.5}$ Flowmeters and Devices

Flow rate standards used for calibrating or verifying a $PM_{2.5}$ sampler's flow rate measurement device must have an accuracy of ± 2%. This flow rate standard must be a separate, stand-alone device designed to connect to the flow rate measurement adapter. The flow rate standard must have its own certification and must be traceable to a NIST primary standard for volume or flow rate.

The following section includes the advantages and disadvantages of some of the various types of flow rate standards that might be considered for $PM_{2.5}$ sampler calibration.

Bubble Flowmeters

Although manually-operated and timed bubble flowmeters are available, a semiautomatic instrument is easier to use and is likely to provide more uniform flow rate measurements. Because the liquid used to form the bubbles is usually water-based, a water vapor correction may be required to compensate for a volume increase due to evaporation of the water in the instrument. Furthermore, the instrument cannot be used below 0°C because the soap solution will freeze.

Piston Flowmeters

Automatic dry-piston flowmeters are relatively easy to use and are not subject to the water vapor correction of the liquid-freezing limitation of the bubble flowmeters. However, they may still be subject to a lower operational temperature limit due to LCD readouts. Alternatively, hard-copy printouts could be used to log results. Some models which are not equipped with a pressure release valve can create a series of momentary pressure drops as the piston is in operation, which the $PM_{2.5}$ sampler may compensate for by increasing the driving force to the pump.

Mass Flowmeters

Although mass flowmeters may be considered as calibration standards, they have a number of shortcomings in this application. They have a high pressure drop, which could change the sampler flow rate or otherwise affect the operation of the sampler. Mass flowmeters also require conversion of the measured mass flow rate to the actual volumetric flow rate for comparison to the $PM_{2.5}$ sampler displayed value. The flow rate measured by the sampler may also have to be corrected to account for significant pressure drop introduced by the mass flowmeter itself. Finally, mass flowmeters are subject to zero or span drift, particularly over the wide range of temperatures encountered at field sites, so their accuracy should be reverified frequently over a wide temperature range.

Orifice Devices

Orifice devices are simple and reliable, but they require corrections for temperature and pressure and may have a significant pressure drop. They also require a very accurate and sensitive differential pressure measurement device, such as a manometer or an aneroid differential pressure gauge, whose accuracy must be reverified frequently. Electronic micromanometers are convenient to use with an orifice device. Readings from electronic micromanometers should be crosschecked against a water manometer prior to a round of sampler verifications or calibrations.

Laminar Flow Elements

Laminar flow elements generally have a lower pressure drop than orifice devices but otherwise have the same requirements and disadvantages.

Wet Test Meters

Wet test meters are generally not practical for field use but may be used for laboratory calibrations.

Dry Gas Meters

Dry gas meters may be considered for field calibration. Some meters may have a substantial pressure drop. They should be checked for leaks and mechanical problems and be recertified at least annually. Dry gas meters may take a much longer period of time to use since instantaneous and semi-instantaneous values are not available.

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Chapter

4

This chapter will take approximately 3 hours to complete.

OBJECTIVES

Terminal Learning Objective

The student will be able to identify the procedures of particulate matter sampling.

Enabling Learning Objectives

4.1 View the principle of inertial collection.
4.2 Identify and classify the inertial sampling devices.
4.3 View collection efficiency and penetration efficiency of inertial sampling devices.
4.4 Identify limitations and sources of error in inertial collection.
4.5 View filtration sampling.
4.6 View gravitational sampling.
4.7 Describe the principles and applications of electrostatic precipitation.
4.8 Describe the thermal precipitators.
4.9 Summarize the fundamental principles for sampling for PM in the atmosphere.

Particulate Matter Sampling

4.1 Introduction

This chapter provides a definition for the subclasses of particulate matter (PM), addresses the rationale for size fractionation of particulates, and discusses particulate matter sampling techniques in ambient air. PM is the generic term for a broad class of chemically, physically, and biologically diverse substances that exist as discrete particles (liquid droplets or solids) over a wide variation in the size of the particles. EPA typically characterizes the physical and chemical characteristics of PM through various pump-based and direct-reading continuous techniques. When suspended in air, PM is typically referred to as "aerosol." Acute and chronic health effects have been positively associated with PM exposure. Because health effects and visibility are related to particle size, concentration, and chemical composition, EPA extensively characterizes PM.

Particles are usually characterized by their size diameter. PM size ranges from molecular clusters of approximately 0.001 micrometers (μm) in diameter to particles of approximately 100 μm. Particles less than about 0.001 μm act more like gases, and thus are not treated as particulate matter; while particles greater than 100 μm, due to their size and mass, are easily removed and are typically not released as an air emission. Because particles are present in many shapes and sizes, EPA methods characterize particles by their aerodynamic diameter, which is defined as the diameter of a sphere with a unit density (density of water= 1000 kg/m^3) that will settle in still air at the same rate as the particle in question.

Particle size is important because of the adverse health effects associated with particles in certain size ranges. The deposition of particles in the respiratory system is shown in Figure 4-1. Basically, the smaller the particle, the more likely it will penetrate deeper in the lung. Particles much greater than 100 μm are typically not inhaled, while smaller particles, typically less than 4 μm, can interfere with oxygen gas-exchange in the lung alveolar region. Figure 4-2 shows the penetration ability of particles in the lung, defined by commonly-used size-based particle terms.

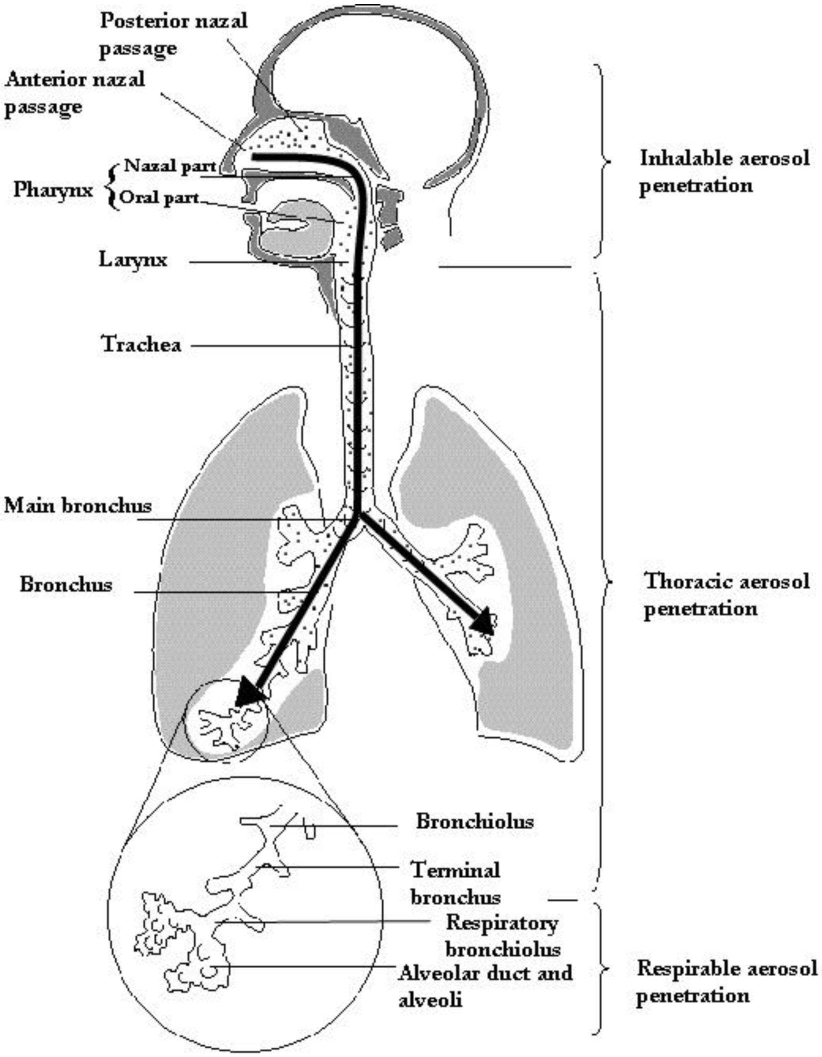

Figure 4-1. Respiratory collection of particles.

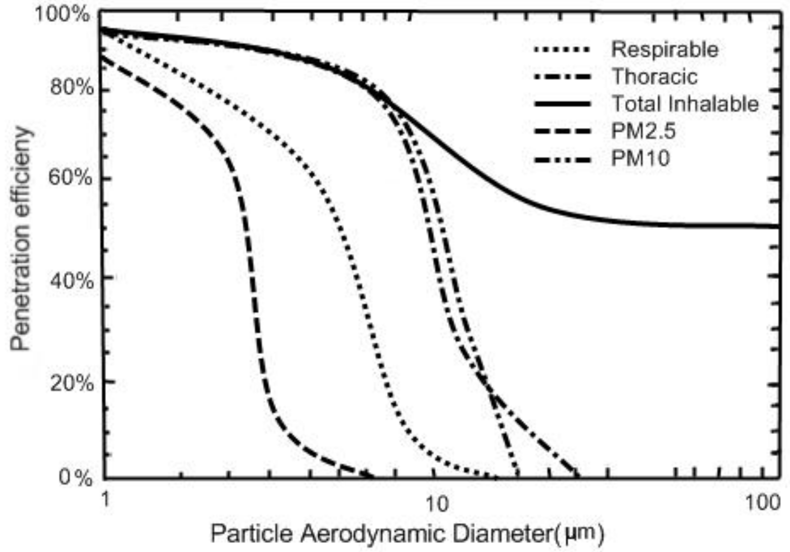

Figure 4-2. Modeled lung deposition as a function of particle size.

Inhalable, thoracic, and respirable particles, which describe where particles are likely to deposit in the lung, are terms used more commonly in industrial hygiene (occupational-related PM exposures), while $PM_{2.5}$ and PM_{10} are terms used by EPA to describe particles up to 2.5 μm and up to 10 μm, respectively. These EPA size fractions are also described with the terms "coarse" (10 μm – 2.5 μm) and "fine" (<2.5 μm). Exposure to large particles can cause coughing and sneezing, while smaller particles can bypass the body's defense mechanisms and disrupt cellular processes.

In addition to being characterized by their size, particles can also be described by their origin or formation mechanism, chemical composition, and physical properties, as well as in terms of what is measured by a particular sampling technique. Figure 4-3 presents particle size distributions of several significant sources of particulate emissions.

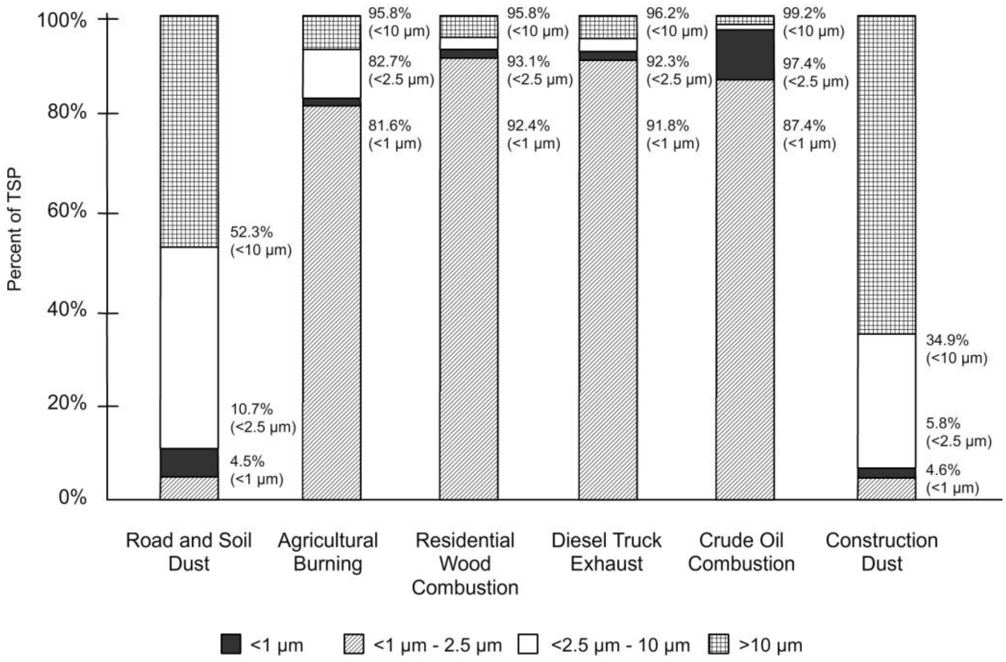

Figure 4-3. Particle size distributions of sources of particulate emissions.

Figure 4-4 shows the idealized size distribution of particles in ambient air (Chow, 1997). More specifically, the figure shows the relative concentration of $PM_{2.5}$, PM_{10}, and TSP size fractions in ambient air. These distinct curves are commonly referred to as "modes." The mass collected is proportional to the area under the size distribution within each size range. Although large particles contribute most to the mass concentration, as shown in Figure 4-4, there are typically many more small particles in ambient air on a number of particles per unit volume basis.

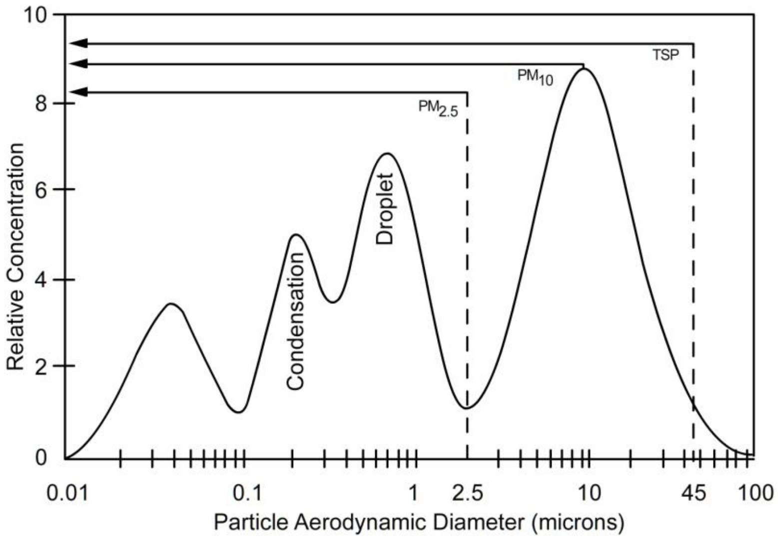

Figure 4-4. Idealized size distribution of particle in ambient air.

Inherent to pump-based sampling, no sampling device is able to collect all particles in a desired size range with 100% efficiency. For example, particle size selection devices, such as a Well Impactor Ninety Six (WINS) or Very Sharp Cut Cyclone (VSCC) used in $PM_{2.5}$ sampling, are designed to collect 50% of particles of 2.5 μm aerodynamic diameter size while allowing the remaining 50% to pass through the device. The collection efficiency of these devices increases at particle sizes greater than 2.5 μm, while particles less than 2.5 μm pass through the device with greater penetration efficiency until finally collected on a collection plate or filter. $PM_{2.5}$ is then determined to be the mass concentration of particles collected on a filter that passed through the WINS or VSCC (collection plates and filters capture particles at ~100% collection efficiency). A detailed discussion on collection and penetration efficiency is provided later in this chapter. Examples of collection efficiency curves for typical PM sampling devices are shown in figures 4-8 and 4-11.

The original National Ambient Air Quality Standards (NAAQS) for particulate matter were first established in 1971, and were measured based on the use of total suspended particulate (TSP) samplers known as high-volume samplers. The high-volume sampler, which is based on a filtration technique, typically captures particles up to 45 μm and usually up to a nominal size of 25 to 45 μm. In 1979, EPA added PM_{10} to TSP as the indicator for particles, where PM_{10} refers to particles with a mean aerodynamic diameter less than or equal to 10 μm. Although the TSP standard was revoked in 1987, TSP measurements continue to be taken for various sampling purposes.

On July 18, 1997, EPA promulgated new PM standards which included NAAQS for particulate matter with an aerodynamic diameter less than or equal to 2.5 μm, referred to as $PM_{2.5}$. In 2006, PM_{10} and $PM_{2.5}$ standards were revised to their current values (Chapter 7).

In this chapter, the discussion of particulate matter sampling will include inertial collection techniques, along with filtration, gravitational, and precipitation techniques. Discussion of sampling devices within each category will be restricted to those commonly used in ambient air sampling. Specific methods for sampling/monitoring of PM will be discussed in Chapter 5.

Principles of Inertial Collection

A number of factors and general principles associated with liquid and solid aerosol particles are helpful in most effectively selecting and using an ambient air sampling device. In addition to the size and nature of the particles, other important aspects to consider include the theory of inertial impaction, particle settling, the effects of thermal and electrical forces, and the theory of filtration. A discussion of these general aspects begins with the topic of inertial collection.

Inertial collectors are designed to give a size-representative sample of particles in the atmosphere using the principle that particles in a gas stream are more dense than the fluid (air) in which they are suspended. A particle moving in an air stream with approximately the same velocity as the air stream has more momentum (mass × velocity) than the volume of air that it displaces because of its higher mass. The momentum, or inertia, possessed by a particle in a moving air stream will cause the particle to be deflected less than the air in the vicinity of the particle when the air stream undergoes a sudden change in direction. Such a deflection will occur when an obstacle is placed directly in the path of an aerosol stream. If the resulting deflection of the particle from the air trajectory around the obstacle is great enough (large angle of deflection), the particle will strike the obstacle. High incident velocities will increase the momentum of particles in the air stream, thereby enhancing their removal. High velocities can be attained by passing the air stream through an orifice (jet) prior to the stream striking the obstacle, as shown in Figure 4-5.

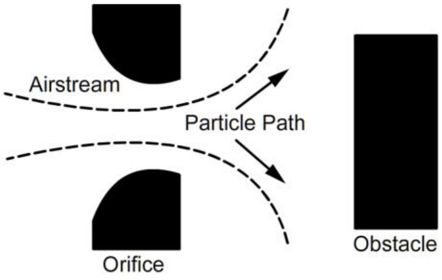

Figure 4-5. Particle collection by impaction.

Under the proper conditions, most of the particles within a certain size range that can be made to strike the obstacle will become attached to and remain on the collection surface.

A practical discussion of inertial sampling devices follows, including examples of numerous particulate matter collectors used in ambient air sampling.

4.2 Inertial Sampling Devices

The inertial collection process is subdivided into two main types: impaction and impingement. The distinction is made by the manner in which the sample material is retained in the sampling device.

Impaction Devices

Impaction devices collect and retain particles from an aerosol stream on a collecting surface. The collecting surface is removed from the instrument and the sample analysis is, in many cases, performed directly on the collecting surface. Particle adhesion is caused primarily by electrostatic attraction and by molecular surface phenomena known as Van der Waals forces. Some loss of large particles occurs with high aerosol velocities. It is believed that in the case of small particles (several micrometers or less), nearly all of those striking the collecting surface are retained on the surface. The collection surface in many impaction devices is coated with a thin film of oil or light grease to aid in particle retention. In some devices, retention is aided by passing the incoming particles through a zone of moisture-saturated air; moist particles adhere more readily to a collection surface. Coating of the plates and water saturation of the particles affect the calibration of an impactor and must be accounted for if the impactor is to be used for determining particle size distributions.

Two-Stage Impactor

Figure 4-6 shows a schematic of a two-stage impactor. The air stream containing the various size particles flows through the first large jet nozzle and impacts on a collection plate oriented perpendicular to the axis of the nozzle. At the first nozzle exit, the air stream is deflected sharply by the collection plate. Larger particles continue forward and are collected on the first plate, while the smaller particles follow the air stream into the second nozzle, which has a smaller jet and a higher velocity, allowing the smaller particles to be collected on the second collection plate.

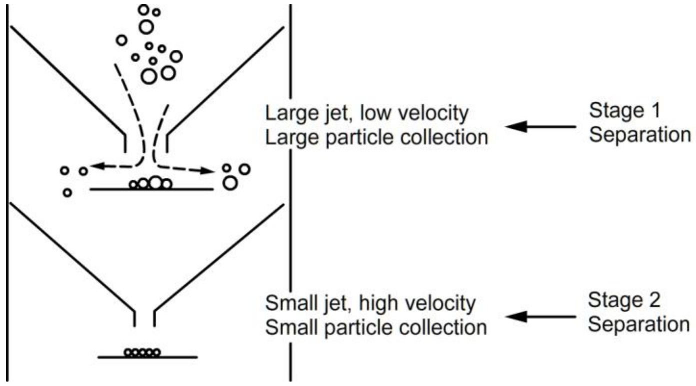

Figure 4-6. Two-stage impactor.

Andersen Cascade Impactor

An example of a multi-stage impactor is the Andersen standard sampler. This sampler usually contains six to eight stages (i.e., collection plates) with numerous, successively smaller, evenly distributed holes (orifices) in each stage. A constant flow rate is maintained through the Andersen sampler which causes the aerosol stream velocity to increase at each stage, resulting in a deposition of particles in size fractions. Each stage of the sampler consists of a perforated disc located above a collection medium (Figure 4-7). The sample air passes through the openings in the disc and must then make an abrupt change of direction over the collection medium. The particles possessing too great a momentum to continue in the air stream are impacted on the collection surface. The collection surface can be coated with a light oil, silicone grease, filter media, aluminum foil, or wax to help increase the collection efficiency. The thickness of the coating is not important, as long as it is at least the thickness of the particle that is to be collected. However, a heavy coating is not recommended since this will likely clog the orifices. Such coatings may also interfere with subsequent chemical analysis and the size ranges of particles collected.

The greatest limitation of the Andersen sampler is the relatively low flow rate, 0.028 cubic meters per minute (1 cubic foot per minute, or cfm), that must be maintained. Such a flow rate limits the amount of sample that can be collected. Figure 4-8 shows the collection efficiency of each stage of the Andersen cascade impactor operated at a flow rate of 1 cfm, over the particle size range of 0.3 μm to 11 μm.

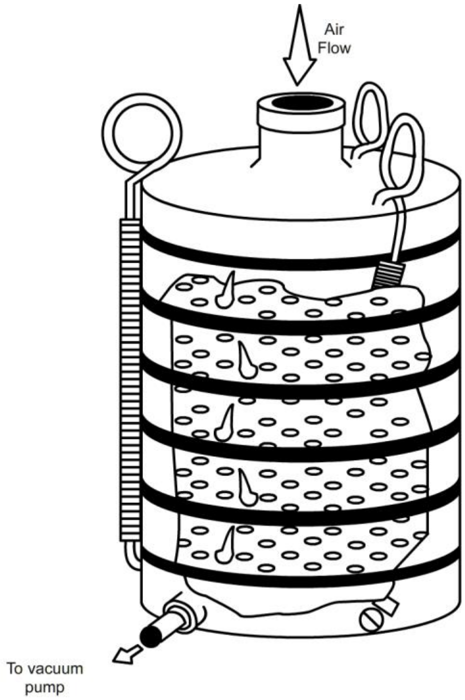

Figure 4-7. Andersen cascade impactor.

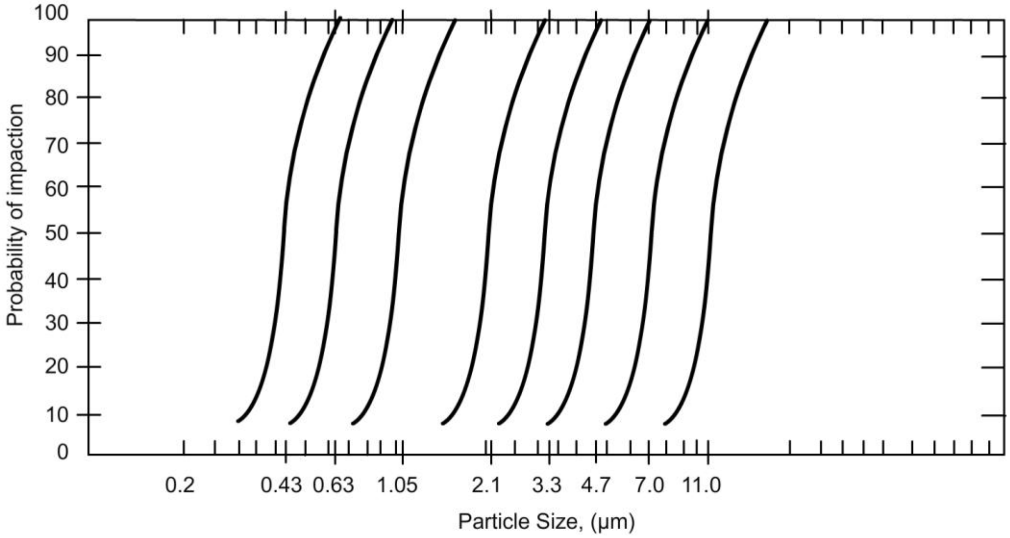

Figure 4-8. Collection efficiency of each of 8 stages (i.e., collection surfaces) of an Andersen cascade impactor operated at 1 cfm.

High-Volume Andersen Cascade Impactor

A modification of the Andersen sampler has led to the high-volume (hi-vol) Andersen impactor, which is typically operated at a flow rate of 0.57 m^3/min (20 cfm). This sampler consists of five stages with the typical Andersen perforated discs. Below the discs are gaskets and collection surfaces (Figures 4-9 and 4-10). The collection surfaces, usually glass fiber filters or aluminum foil, are supported by the plates themselves; i.e., the collection surface for plate 1 is supported by plate 2, and so on. To allow unrestricted aerosol flow, the collection surface has holes that line up with the orifices of the plate supporting it. The five stages are held together by a central bolt and are aligned by four evenly spaced rods. The impactor is mounted on a hi-vol sampler. An 8- by 10-inch filter mounted on the hi-vol sampler is the back-up filter for the impactor. Figure 4-11 shows the collection efficiency of the hi-vol Andersen impactor operated at 20 ft^3/min over the particle size range of 0.75 μm to 8 μm.

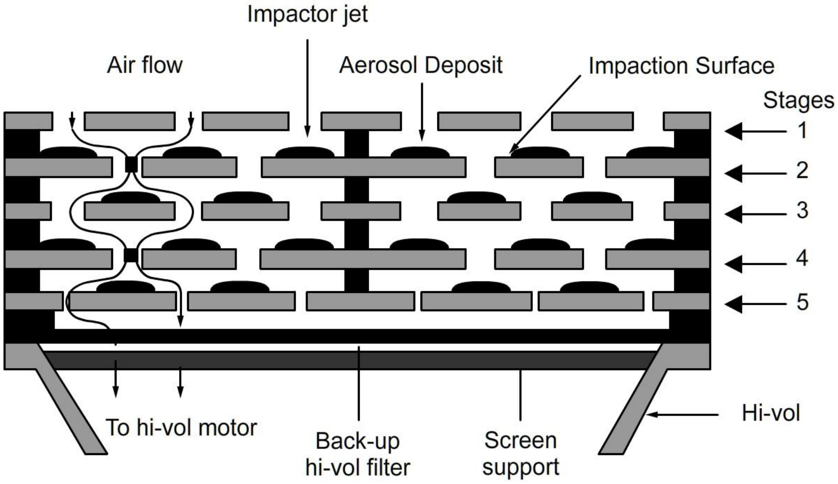

Figure 4-9. Cross-sectional view of a hi-vol Andersen impactor.

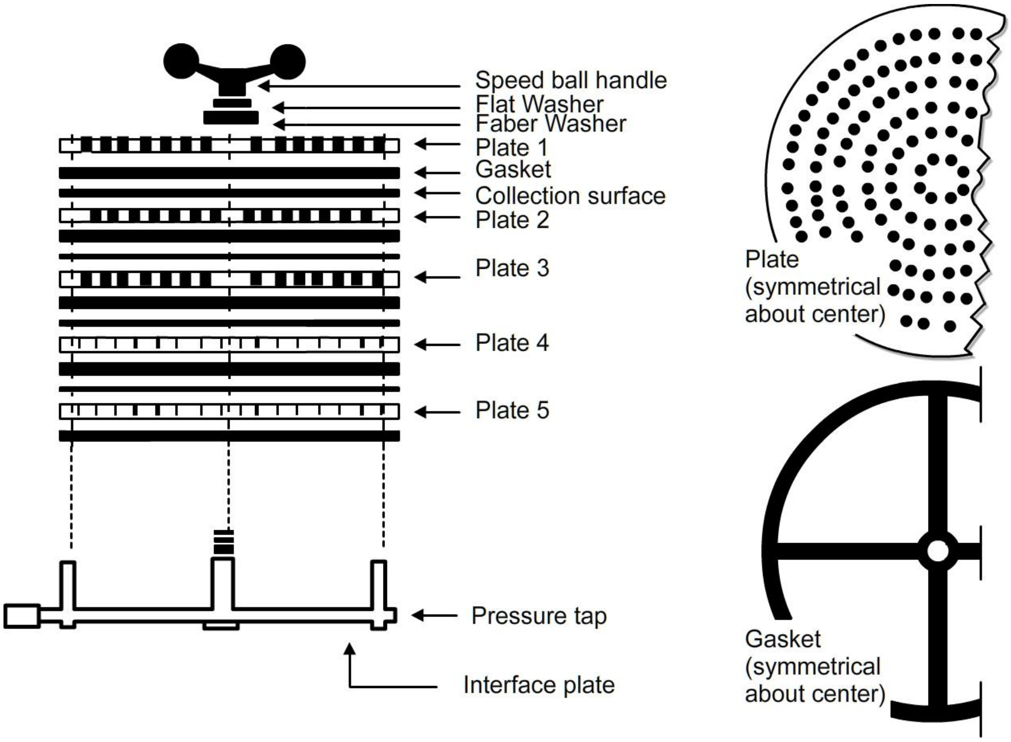

Figure 4-10. Expanded view of a hi-vol Andersen impactor.

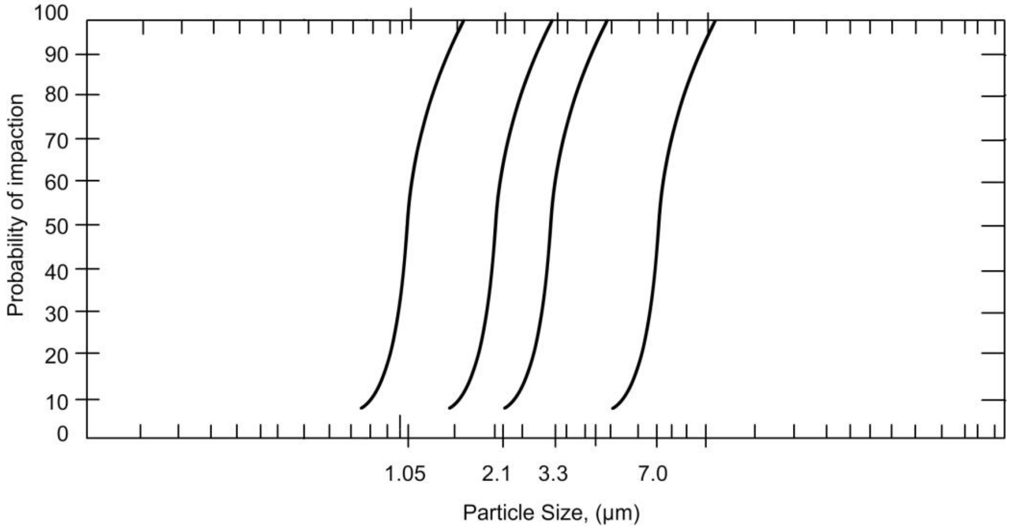

Figure 4-11. Collection efficiency of a hi-vol Andersen impactor operated at 20 cfm.

Multiple-Slit High-Volume Cascade Impactor

Another high-volume cascade impactor utilizes a typical high-volume sampler with an adapter comprised of six stages with successively smaller slit openings. Behind each slit is a filter for retaining particles. The sixth stage of this impaction device uses a typical hi-vol filter for collection of small particles.

The air sample is drawn through the slits and collection filters (Figure 4-12). The slits become increasingly narrower, thus causing the velocity to increase at each stage so particles of decreasing size are impacted on each successive filter. The distance from the slits to the collection filter becomes smaller with each stage to increase the collection efficiency. This impactor incorporates the advantage of hi-vol sampling (high flow rate [1.13 m^3/min, 40 cfm] and, therefore, large sample size) and the advantage of impactor sampling (particle sizing).

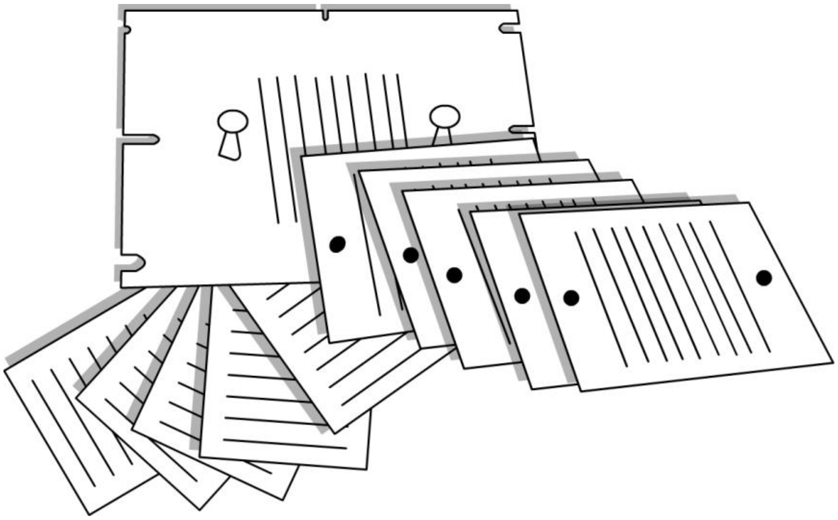

Figure 4-12. Multiple-slit high-volume cascade impactor.

Automated Cascade Impactor

Cascade impactors that provide somewhat real-time particulate matter concentrations have been developed by using oscillating quartz crystals as impaction surfaces. Particles impacting on the crystals cause their oscillation frequencies to change. The amount of change in frequency of a crystal is proportional to the mass of the particles collected on the crystal. Therefore, this relationship can be used to measure particle concentration. However, the proportional relationship is only valid over a certain frequency range and depends on the physical characteristics of the particles collected (e.g., dry versus sticky). One such impactor is depicted in Figure 4-13. It provides concentration measurements for particles in ten size ranges (from 0.5 to 35 μm) by using ten impactor stages, each having an oscillating quartz crystal that is connected to the sampler's electronic display.

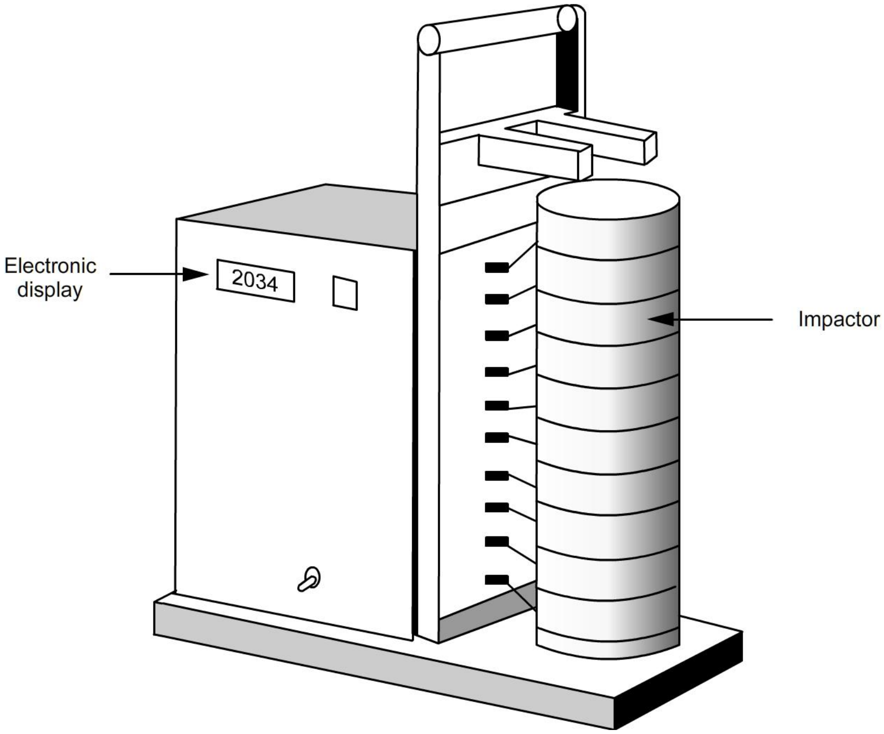

Figure 4-13. Quartz crystal cascade impactor.

PM$_{2.5}$ Inertial Particle Size Separator

EPA's Federal Reference or Federal Equivalent Method (FRM or FEM) sampler for PM$_{2.5}$ provides for the measurement of the mass concentration of particulate matter with an aerodynamic diameter less than or equal to a nominal 2.5 μm in ambient air over a 24-hour sampling period. A Well Impactor Ninety-Six (WINS impactor) configured in EPA-approved samplers is an EPA FRM for sampling PM$_{2.5}$ (see Chapter 5 for FRM and FEM designation criteria). In 2006, the EPA approved the Very Sharp Cut Cyclone (VSCC) as a FRM alternative to the WINS impactor when used in EPA-approved samplers. The FRM sampler pulls ambient air at 16.67 lpm into a specially-shaped inlet and through a WINS impactor or VSCC, where the suspended particulate matter in the PM$_{2.5}$ size range is separated for collection on a polytetrafluoroethylene (PTFE) filter, also known as a Teflon® filter. Figure 4-14 shows the inlet of the sampler, which only allows for the collection of particles less than 10 μm. Figure 4-15 illustrates the WINS particle impactor and filter holder assembly. The well of the assembly contains a 37 mm diameter glass fiber filter that is immersed in 1 mL of low volatility, low viscosity diffusion oil. The oiled glass fiber filter helps remove particles between 2.5 and 10 μm in diameter by preventing the bouncing of the incoming particles off the loaded impactor. Oil used in the WINS impactor can crystallize in cold environments, therefore allowing particles greater than 2.5 μm to collect on the PTFE filter.

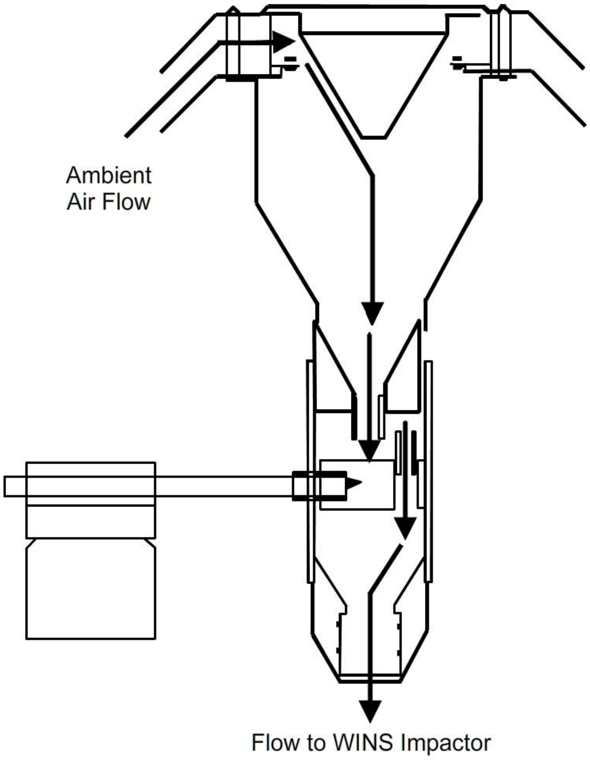

Figure 4-14. Inlet of $PM_{2.5}$ inertial particle size separator.

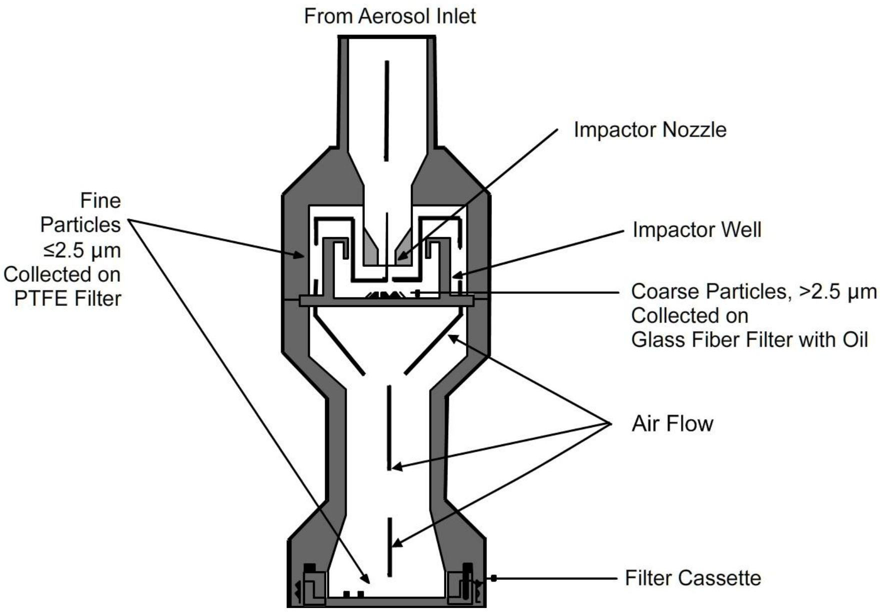

Figure 4-15. WINS particle impactor and filter holder assembly.

Impingement Devices

Impingement devices differ from impactors because the jet and striking surface are immersed in a collecting fluid such as water. The particles that are removed from the aerosol stream are wetted by and retained in the fluid. Most impingers in use are variations of the instrument developed by Greenburg and Smith (Balzer 1972). The Greenburg-Smith type of impinger consists of a glass cylinder with a small concentric glass tube insert. A glass jet and impingement plate are attached to one end of the tube, which is immersed in the collecting fluid. These impingers collect a sample at flow rates of about 0.1 to 1 ft^3/min.

Impingers are most commonly used in collecting dusts, mists, and fumes in the evaluation of occupational health hazards. In addition to collecting soluble gases and particulate matter, the Greenburg-Smith impinger efficiently collects insoluble particles that are greater than 2 μm in diameter.

Centrifugal Separation Devices

Centrifugal separation is a variation of the inertial collection process in which particles are removed from an air stream by the centrifugal force created by moving an aerosol rapidly through a circular path.

Several types of sampling devices employ the principle of centrifugal separation.

Cyclone Samplers

Cyclone samplers are small versions of the large cyclones used in air cleaning. The cyclone shown in Figure 4-16 contains no moving parts and is designed so that air drawn through it moves in either a circular or a helical path of decreasing radius, thereby increasing its collection efficiency for small particles. As the gas stream surges through the cyclone, particles are separated at the inside surface of the cyclone's wall where the gas velocity approaches zero due to the created centrifugal force. In most cyclone samplers, the particles adhere to the wall or drop into a collection space below the cyclone's chamber.

Most cyclones are not efficient collectors of particles, having diameters less than 2 or 3 μm, depending on particle density. However, small cyclones can be designed to collect particles below 1 μm in diameter. The collection efficiency of a cyclone sampler is strongly dependent on flow rate.

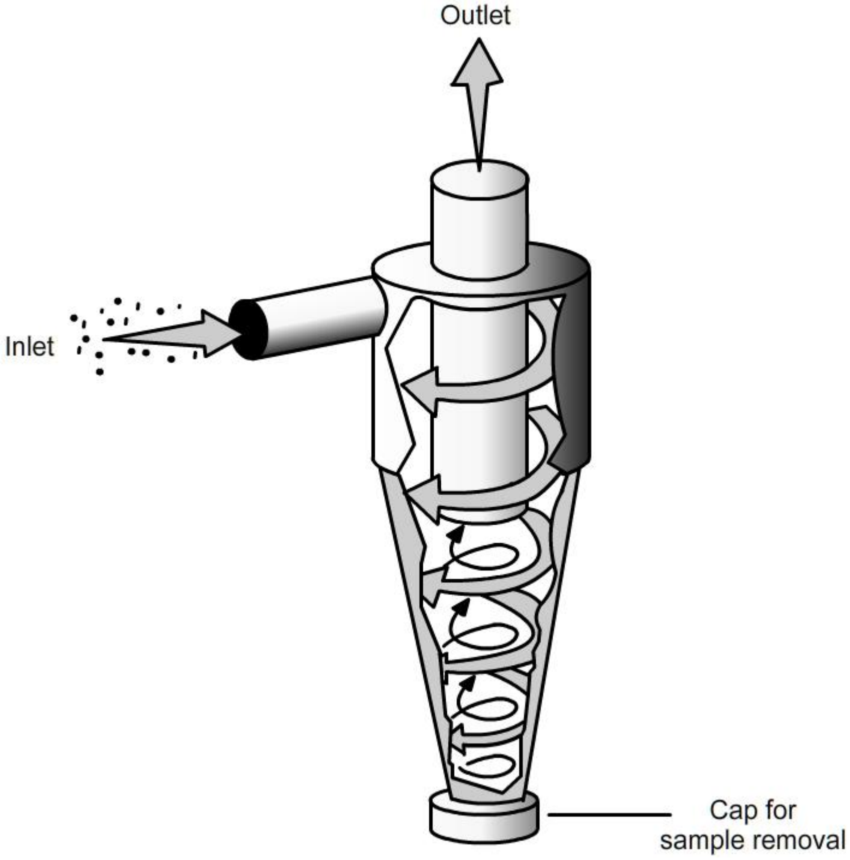

Figure 4-16. Cyclone sampler.

The Very Sharp Cut Cyclone (VSCC) $PM_{2.5}$ fractionator is a centrifugal separation device used to collect $PM_{2.5}$. The flow schematic of the VSCC is shown in Figure 4-17.

The VSCC can be used in place of WINS impactors in EPA-approved samplers, and obtained dual Federal Reference Method (FRM) and Federal Equivalent Method (FEM) status on December 18, 2006. Prior to this date, VSCCs used in these samplers were designated as a FEM (see Chapter 5 for FRM and FEM designation criteria). The VSCC $PM_{2.5}$ fractionator penetration efficiency is very similar to that of the EPA-designed WINS $PM_{2.5}$ impactor (Figure 4-18); however, no oil is used in the VSCC. Consequently, it is preferred over the WINS impactor in cold environments where WINS impactor oil can crystallize. Operation of the VSCC is limited to 30 days of operation between cleanings.

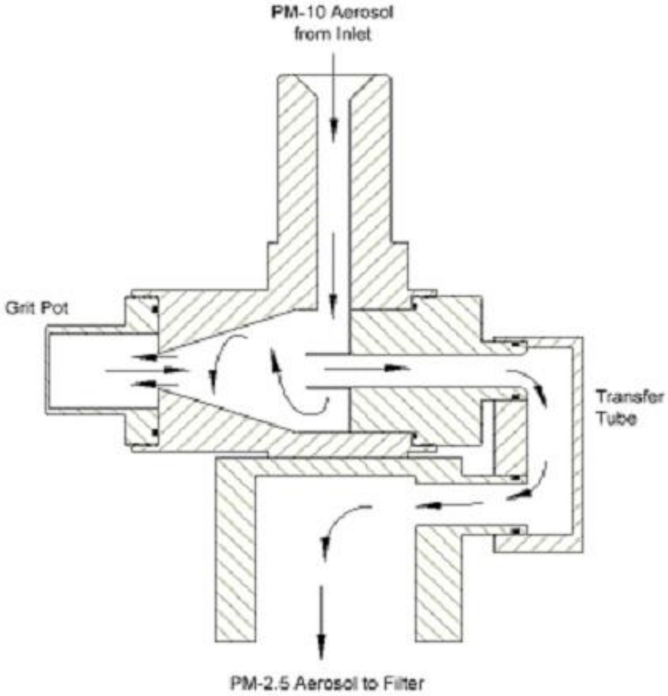

Figure 4-17. Flow schematic of VSCC $PM_{2.5}$ fractionator.

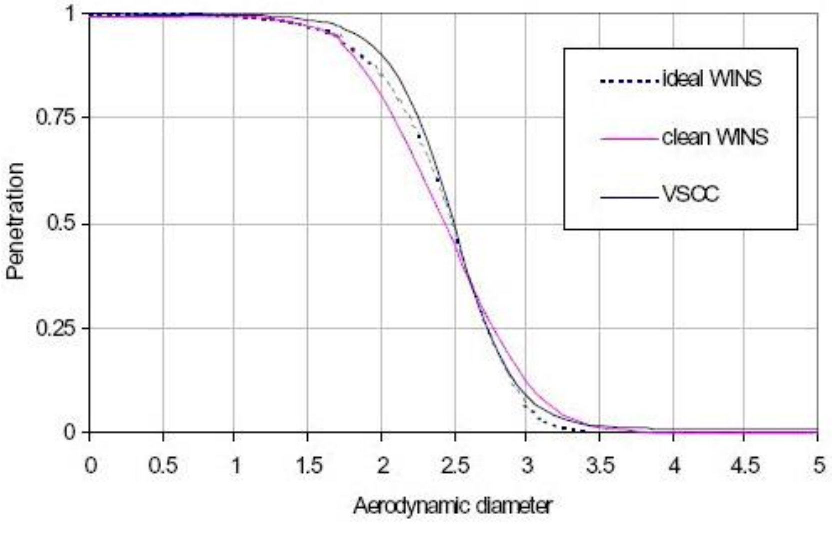

Figure 4-18. Penetration efficiency of VSCC $PM_{2.5}$ fractionator and WINS $PM_{2.5}$ impactor.

Virtual Impactors—Dichotomous Sampler

In the virtual impaction method, instead of the larger particles impacting onto a solid collection surface, they impact into a slowly pumped void and are later collected on a filter downstream. Thus, these larger particles impact through a non-existent void, or virtual surface. As depicted in Figure 4-19, the smaller (fine) particles follow the streamlines of the faster flow (F_f); the larger (coarse) particles are impacted into the slower flow (F_c). A small fraction of the fine particles is impacted and collected with the coarse particles. This can be mathematically corrected when determining fine and coarse particulate concentrations.

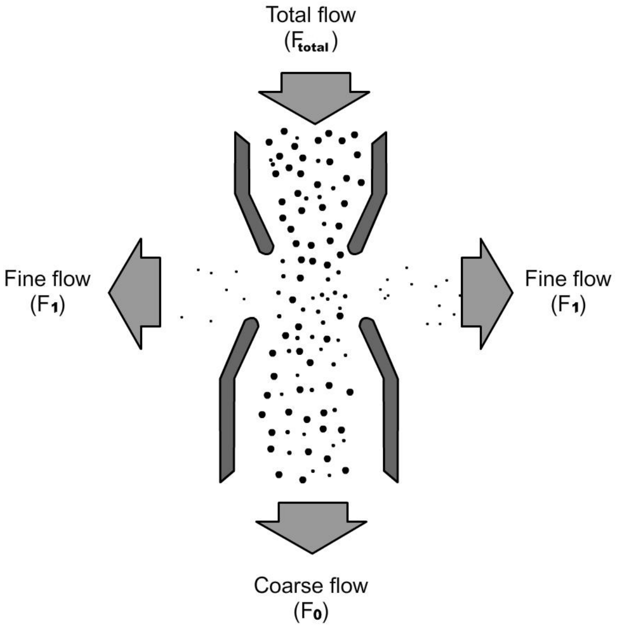

Figure 4-19. Schematic of virtual impactor.

The most recent use for virtual impaction has been in the EPA's efforts to develop a sampler that will separate and collect particulate matter both above and below a 2.5 μm aerodynamic diameter. These efforts have led to the development of the dichotomous sampler. As its name implies, the dichotomous sampler separates particles into two size ranges: fine particles (less than 2.5 μm aerodynamic diameter) and coarse particles (2.5 to 10 μm aerodynamic diameter), as shown in Figures 4-20 and 4-21. Dichotomous samplers use lower flow rates than other PM_{10} samplers and smaller PTFE (Teflon®) filters.

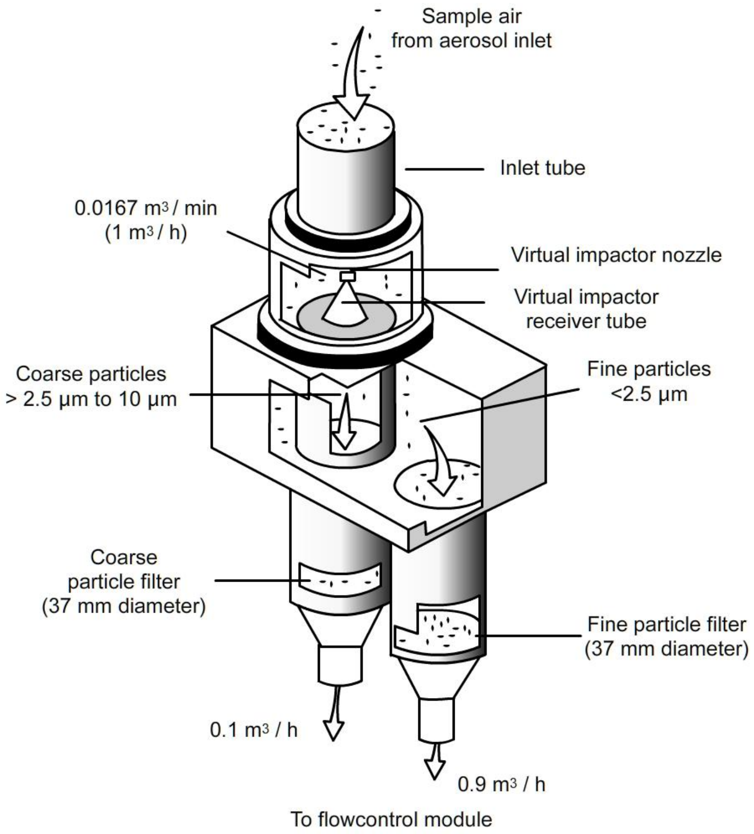

Figure 4-20. Diagram of the sampling module of a dichotomous sampler.

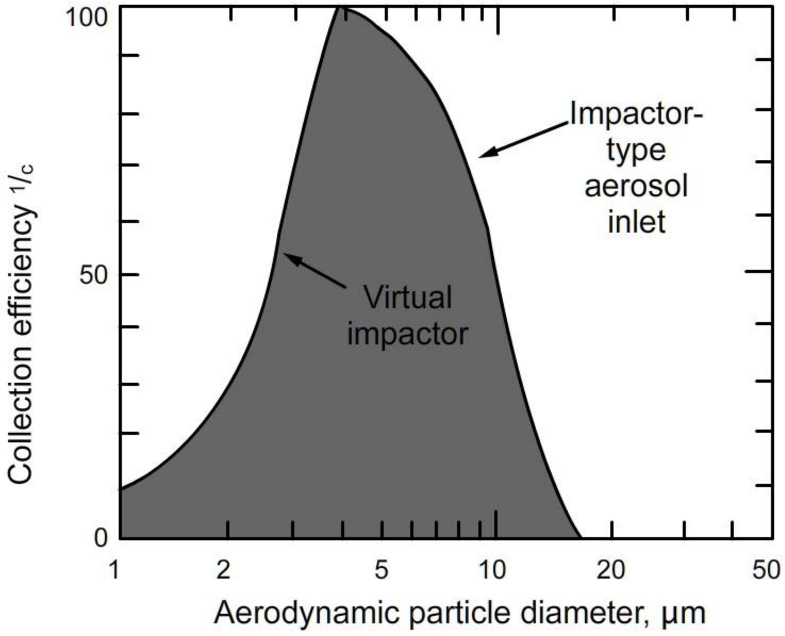

Figure 4-21. Collection efficiencies for a dichotomous sampler.

Virtual impactors have several advantages over conventional impactors:

- Problems associated with conditional impaction, such as particle bounce and reentrainment, nonuniform particle deposition, and cumbersome sample handling, are essentially eliminated.
- Uniform particle deposition onto the filters is ideally suited for photo-excited x-ray fluorescence (a nondestructive chemical analysis technique) and beta-gauge mass measurement.
- No grease or oil is needed to improve collection efficiency (this reduces potential sample contamination).
- Filters can be chosen to eliminate or minimize interferences.

Teflon® membrane filters are normally used to collect both coarse and fine particles because of the following advantages:

- Their collection efficiency for particles above 0.01 μm is greater than 99%.
- They have an extremely stable mass for high gravimetric accuracy.
- They have a negligible tendency to absorb or react with gases (therefore, low artifact formation of nitrate and sulfate).
- They contain minimal impurities to interfere with analyses for chemical and elemental species.
- They have low mass-per-unit area (desirable for gravimetric, x-ray fluorescence, and beta-gauge measurements).

However, these Teflon® membrane filters will not support themselves; therefore, they are bonded to a thin annular polyester ring.

Two aerosol inlets are available for providing 10 μm cut points (50% collection efficiencies) for dichotomous samplers. One type functions as a single-stage impactor (Figure 4-22). After entering the inlet and passing through a bug screen, particles in the sample air are accelerated as they pass through a nozzle to an impactor target module. Because of their momentum, particles having diameters greater than the inlet's 10 μm cut point impact onto the surface (target) of the impactor module. Smaller particles rise through the impactor module and pass to the virtual impactor of the dichotomous sampler. The other aerosol inlet uses a cyclone to remove particles having diameters greater than its 10 μm cut point from the sample air before the air enters the virtual impactor. Because of their symmetrical designs, both inlets are wind-direction insensitive. Also, wind speeds from 2 to 24 km/hr have a negligible effect on the cut point of both inlets.

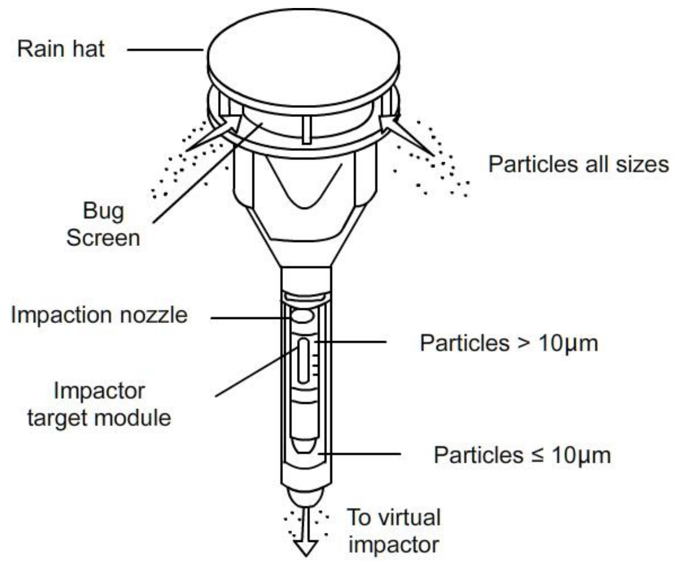

Figure 4-22. Impactor-type aerosol inlet for dichotomous sampler.

Figures 4-23 and 4-24 depict a manual dichotomous sampler. Samplers that automatically change fine and coarse particle filters at preset time intervals are also commercially available.

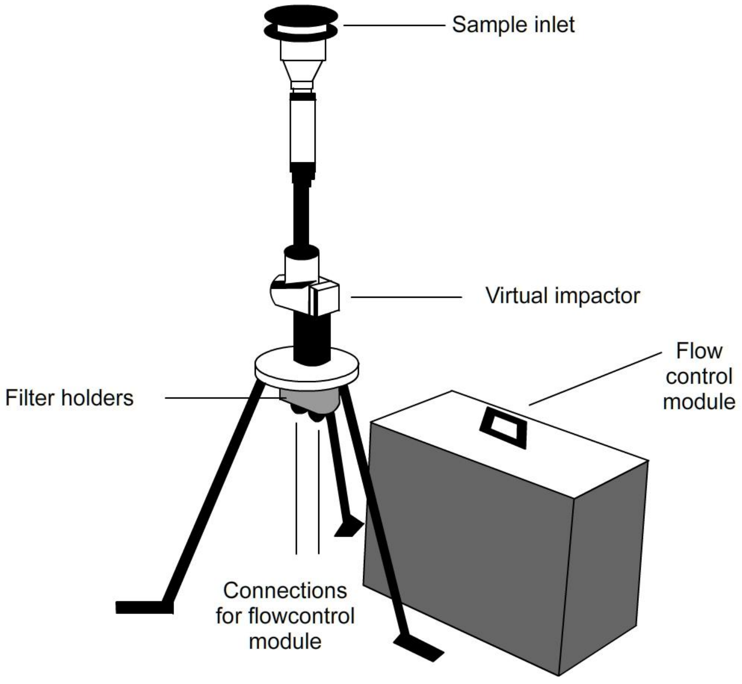

Figure 4-23. Dichotomous sampler.

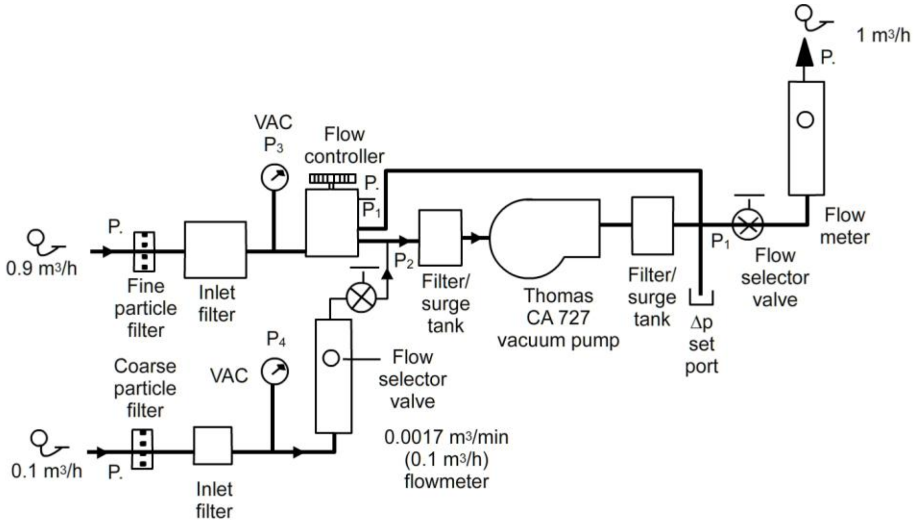

Figure 4-24. Flow schematic of dichotomous sampler.

4.3 Collection Efficiency and Penetration Efficiency of Inertial Sampling Devices

Though the principle is the same for all types of inertial sampling devices, the parameters associated with collection efficiency are somewhat different for the basic single-stage or cascade impactor than for the air centrifuge or cyclone. The discussion in this section is confined to the jet type of impactor, and this discussion may not be applicable to other types without modification. In this section, discussions of particle size refer to the aerodynamic diameter or Stokes diameter, unless otherwise stated. The aerodynamic diameter is the diameter that a unit density particle of spherical shape would have if it behaved the same as the particle being studied. The Stokes diameter for a particle is the diameter of a sphere that has the same density and settling velocity as the particle being studied. The collection efficiency of an impaction device is a function of several parameters (discussed later in this section).

Definition of Collection Efficiency and Penetration Efficiency

The collection and penetration efficiency of an impaction device can be described by the ratio of the number of particles striking an obstacle to the number that would strike if the stream lines were not deflected.

For the purposes of this discussion, collection efficiency will simply be defined as the fraction of the particles in an incident aerosol stream that is retained on the collection surface of the sampling device. Penetration efficiency will be defined as the fraction of the particles in an incident aerosol stream that passes through the collection surface of the sampling device. Essentially, collection and penetration efficiencies are opposites.

The collection efficiency of impaction can be plotted as a function *I*, the inertial impaction parameter, to give a collection efficiency curve for an impaction device. Collection and penetration efficiencies can be calculated for individual devices such as the WINS and VSCC (Figure 4-18), and for multi-stage devices such as the Andersen sampler (Figure 4-8) and high-volume Andersen sampler (Figure 4-11).

Impactor Performance Characteristics

Instead of plotting efficiency of impaction against *I*, it can be plotted against particle size for a given device, since *I* is a function of particle size and several other parameters. The efficiency of impaction when plotted against particle size follows a sigmoid (or S-shaped) curve, such that there is a minimum size below which no particles are collected and a maximum size above which all particles are collected. For a well-designed impactor, the range between these two sizes is sufficiently narrow that a functional size separation is made. The most effective way to describe the ability of an impactor stage to separate particle sizes is to show the efficiency of collection as a function of size.

Properties of Aerosols Affecting Inertial Collection Efficiency

For a given collection device, several properties of the *aerosol* affect the efficiency of collection:

Particle Size

For any device there is a minimum particle size below which no particles are collected and a maximum particle size above which all particles are collected or removed from the sampling stream. Above 50 μm, some particle loss occurs by impaction on the walls of the sampling device. Particles and droplets greater than about 200 μm are seldom found on the sample collection area because they are shattered or lost on the walls of the device. Particles below about 0.5 μm in diameter are difficult to collect with impaction devices because their momentum is not appreciably different from that of the air. Consequently, under many sampling configurations, particles in this size range are able to deflect obstacles in a similar manner as air molecules. Most impacting devices have a high collection efficiency for particles with diameters greater than 0.5 μm. Collection efficiencies of nearly 100% are claimed for several impaction devices for particles in the size range from 0.5 to 10 μm.

Particle Density

Impaction devices are efficient collectors of high density particles; they have been used to selectively sample work atmospheres of plutonium dusts. Sub-micrometer particles of high density can be efficiently collected, since they are equivalent to unit density particles of much greater size.

Aerosol Fluid Properties

The physical properties of the gas in which the particles are dispersed will affect the collection efficiency of an inertial collector. For example, any factor which affects the gas's viscosity, such as temperature, will in turn affect the collection efficiency.

Properties of the Collecting Device Influencing Collection Efficiency

Impactors and impingers are designed for sampling a variety of aerosols. Collection efficiency for a particular aerosol can be optimized by design considerations.

Jet Size

The impaction jet size will influence the collection efficiency by affecting the velocity with which the incident air stream strikes the collection surface. As jet size decreases, the impaction velocity increases, as shown in Equation 4-1.

(Eq. 4-1) $$v = Q/A$$

Where:
v = *air velocity*
Q = *volumetric flow rate*
A = *cross-sectional area of the air stream*

In a multi-stage impaction device, jet velocities range from several meters per second in the first stage to greater than 50 meters per second in the last stage. The corresponding jet cross-sectional areas range from about 70 mm^2 in the first stage to less than 5 mm^2 in the last stage in a typical multi-stage impaction device.

Multi-stage impaction devices are available at a variety of flow rates. Flow rate and design characteristics will greatly influence the collection efficiency of an air sampling device.

Jet Shape

Studies of impaction efficiency showed only small differences in collection efficiency between round and rectangular jets.

Jet to Collection Surface Distance

The distance between the jet opening and the collection surface controls the degree of deflection of the aerosol stream. By decreasing the distance between the jet and the collection surface, the angle of deflection of the aerosol stream is increased. A large deflection angle is required to remove the smaller particles from an aerosol stream. In the common cascade impactor with a single jet at each stage, the distance from the jet to the collection surface is decreased at each successive stage.

Collection Surface

Detailed studies of collection efficiency as a function of the shape of the collecting surface have been performed for spherical, cylindrical, and flat surfaces with round and rectangular shapes. For most applications, flat collection surfaces are used because particle retention is greatest on these surfaces and microscope slides are sometimes required in collections for particle size analysis.

4.4 Limitations and Sources of Error in Inertial Collection

Inherent Errors in Sample Collection

Inertial impaction is the dominant particle collection method in collection-plate and filter-based samplers. Although inertial impaction is widely used, there are several inherent sources of error in the impaction process that should be understood by individuals involved with the sampling and analysis of PM. These limitations are discussed below.

Particle Shattering

Large particles (greater than 200 μm) and agglomerates are readily shattered upon impaction, and, at the high velocities attained in some impaction devices, particles with diameters as small as two or three micrometers can be shattered. In studies where the number of particles per unit volume of air is of interest, shattering of particles upon collection results in erroneously high results. In size distribution studies, there will appear to be fewer large particles and more small particles than actually exist in the aerosol.

Particle Bounce, Reentrainment of Particles, and Wall Loss

Particle bounce occurs when a particle strikes, but bounces off of the filter, collection plate, or another collected particle. If too much particulate matter collects on the sample collection surface, subsequent particles that are supposed to impact on collection surfaces may be lost by reentrainment when they strike particles already collected. Specifically, phenomenon called "ghost depositing" can occur when particles bounce off the collection area and are redeposited by eddy currents a few millimeters on either side of the sample. When aerosols containing mists or droplets are being sampled, care must be taken to avoid collection of too much material. If too many droplets are collected, they will merge on the collection surface. The individual drops will be lost for size analysis and some material may be lost by run-off.

At high impaction velocities, a small fraction of the particles collected may be reentrained in the air stream. This occurs most often with fragments of large particles that have shattered upon striking the collection surface. Some of the pieces of the shattered particles may be lost from the sample by impacting on the walls of the instrument. A few of the large particles may impact directly on the walls of the instrument and as a result are not collected. Generally, particle bounce, particle reentrainment, and wall loss lead to less than true concentration estimates of PM.

Limited Sample Quantity

The small quantity of sample collected also restricts the choice of analytical methods to those with high sensitivity. Care must be taken to preserve all sample material intact, since with only a few micrograms of sample, the loss of any particulate matter becomes significant.

Some types of inertial samplers, such as cyclones, are not so limited in this respect. Some of these can collect gram quantities of particulate matter.

Poor Particle Resolution for Size Analysis

Particles that collect close to and on top of each other will introduce error in concentration and size studies through the inability to distinguish between individual particles and clumps of particles when examined optically. However, if a representative portion of the collected material is properly remounted, these problems can be minimized.

Errors Associated with the Calibration of Collection Devices

All PM collection devices must be calibrated before obtaining particle size or mass distribution information. Specifically, the particle collection efficiency as a function of the desired parameter (e.g., size or mass) must be determined. One method of calibration is to determine empirically the collection efficiency in the laboratory. In this procedure, a known quantity of a monodisperse aerosol (a gas stream with only one size particle suspended in it) is passed through the impactor or other collection device at a manufacturer-specified flow rate. For cascade impactors, the amount of material collected on each stage is weighed. By varying the size of the monodisperse aerosol, the cut points for each collection device or cascade impactor stage can be determined.

Detailed studies of theoretical collection efficiencies for several types of impaction devices have been performed. The efficiency curves that have been derived for several types of impactors show varying agreement with experimental curves. These curves are usually given in terms of an inertial collection parameter or equivalent particle size such as the one in Figure 4-8. If a particular curve is to be used in a sampling application, the user should be satisfied that the curve is valid for that particular application. Most commercially available inertial samplers are provided with a curve of collection efficiency. In most cases, the methods used to obtain these curves will not be known to the user. Without specific knowledge of the manner in which the curves were obtained, care should be exercised in the application.

Errors in Sample Analysis

PM samples from inertial collection devices can be analyzed in several ways, ranging from simple gravimetry (weighing) to advanced chemical processes such as ion chromatography. The error associated with the analytical procedure should be considered in the overall error assessment of the sampling procedure. The information desired in an investigation may require the use of an inertial collection device, which in turn may limit the choice of analytical procedure. The reverse could also occur; i.e., the information desired, such as particle distribution, may dictate the use of an impaction device to collect the sample. One should be aware of the limitations and errors associated with each analytical procedure that is considered.

Size-Selective Inlets and Devices for Aerosol Sampling

As discussed earlier in this chapter, numerous size-selective inlets and devices are available for particulate matter sampling. A sampler inlet is the initial piece of equipment where particulate matter enters the sampler. An example of a size-selective inlet is a PM_{10} hat placed on a high-volume sampler (Figure 4-25). This size-selective inlet has a similar collection efficiency curve as the VSCC and WINS, but with 50% collection at 10 µm. The VSCC and WINS are examples of size-selective devices for $PM_{2.5}$ (discussed previously). The particular choice of size-selective inlet and device is generally made based upon a number of concerns such as monitoring objective, particle size, and expected particulate matter concentrations. An excellent summary of available devices is addressed in the draft "EPA Guideline on Speciated Particulate Monitoring" (Chow 1997). Table 4-1 taken from this guideline shows the variety of size-selective inlets available, the inlet manufacturer, operating principle, the cut point, and flow rate, with selected comments.

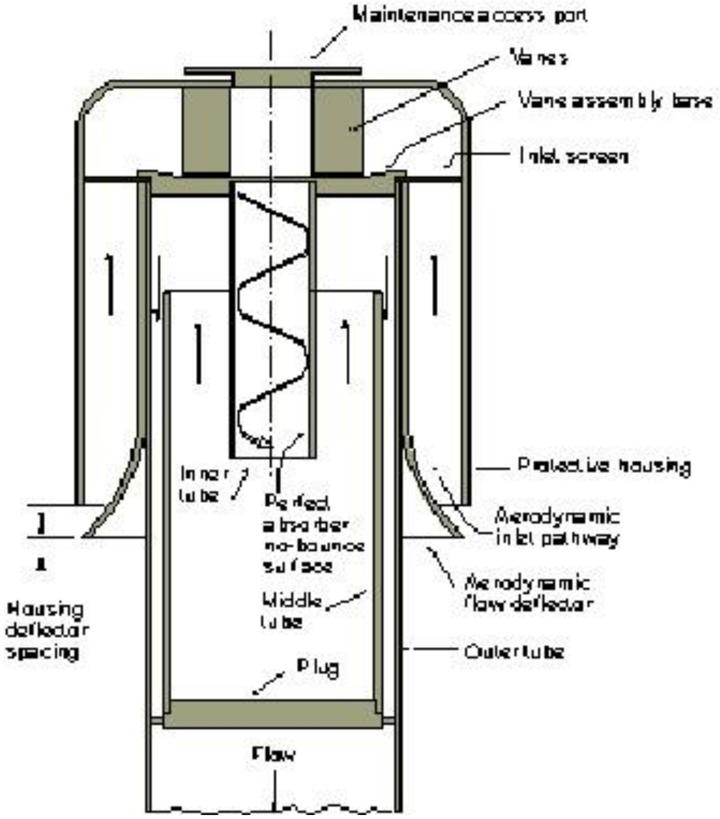

Figure 4-25. High-volume sampler with PM_{10} inlet.

Table 4-1. Size-selective inlets for aerosol sampling.

Inlet Identifier (Manufacturer)	References	Operating Principle	d50 (µm); Slope (no unit)	Flow Rate (L/min)	PM_{10} Reference of Equivalence Reference No.	Comments
High-Volume						
SA[a] or GMC[c] Model 320 (Graseby Andersen, Atlanta, GA)	McFarland et al. (1980)	Impactor	15; 1.5	1,133	None	Single-stage, not greased shim.
SA or GMW Model 321A	McFarland and Oritz (1984); Hayes et al. (1988)	Impactor	10.2; 1.45	1,133	RFPS-1287-065	Two-stage with greased shim.
SA or GMW Model 321B	Hayes et al. (1988); McFarland and Ortiz (1987)	Impactor	9.7; 1.40	1,133	RFPS-1287-064	Two-stage with greased shim.
SA or GMW Model 1200	Purdue (1988); Wedding et al. (1988); Mathai et al. (1988); Hoffman et al. (1988); Hayes et al. (1988)	Impactor	9.7; 1.40	1,133	RFPS-1287-063	Single-stage with greased shim (body hinged).

GMW Wedding PM$_{10}$ (General Metal Works, Village of Cleves, OH)	Woods et al. (1986)	Cyclonic Flow	8.8; --	1,133	None	No inlet cleaning port.
Wedding IP$_{10}$PM$_{10}$ (Wedding & Associates, Fort Collins, CO)	Wedding and Weignand (1985); Woods et al. (1986)	Cyclonic Flow	9.6; 1.37	1,133	RFPS-1087-062	Inlet cleaning port on top of inlet.
Medium-Volume						
SA 254 Medium-Volume PM$_{10}$ Inlet	Olin and Bohn (1983)	Impactor	10; 1.6[d]	113	RFPS-0389-071	Several small screws must be removed to clean.
Wedding Medium Flow PM$_{10}$ Inlet	Wedding et al. (1983)	Cyclonic Flow	9.5; 1.12	113	None	Has a cleaning port. Can use a bottle brush to clean.
Bendix 240 Cyclone (Sensidyne, Inc., Clearwater, FL)	Chan and Lippman (1977); Mueller et al. (1983)	Cyclonic Flow	2.5; 1.7	113	None	Plastic cup acts as a hopper to collect large particles

Low-Volume						
SA 246B	McFarland and Ortiz (1984); Van Osdell and Chen (1990)	Virtual Impactor	10.2; 1.41	16.7	RFPS-0789-073 EQPM-0990-076	Top unscrews to allow access to impaction surface.
Sierra-Anderson 224 and 245	McFarland et al. (1978); Olin (1978)	Virtual Impactor	2.5; --	16.7	None	Virtual impactor can be re-assembled backwards when taken apart for cleaning.
AirMetrics Inc. (Springfield, OR)	Chow and Watson (1996)	Direct Impactor	10; 2.5	5; 5	None	Nylon impactor needs to be cleaned and regreased after every 72 hours of sampling.
WINS (Well Impactor- Ninety Six)	U.S. EPA (1997b)	Direct Impactor	2.5; 1.18^d	16.7	None	Inlet used in $PM_{2.5}$ FRM.
USEPA/HEAD Impactor	Koutrakis et al. (1990)	Direct Impactor	2.1; 1.08^d	10	None	Oiled glass impactor needs to be replaced after every 24 hours of sampling.

Wedding TP_{10}	Wedding et al. (1982)	Cyclonic Flow	9.9; 1.32[d]	16.7	EQPM-0391-081	Plastic cap acts as a hopper to collect large particles.
Bendix Unico 18	Chan and Lippmann (1977)	Cyclonic Flow	2.5; 1.83[d]	18	None	
AIHL Cyclone (Air & Industrial Hygiene Laboratory, Berkeley, CA)	John and Reishcl (1980)	Cyclonic Flow	2.2; 1.87[e] 2.5; 1.38[e] 3.5; 1.40[e]	26.6 21.7 15.4	None	Screw-on cap acts as a hopper to collect large particles.
Stacked Filter Unit (Corning CoStar [formerly Nuclepore Corp.], Cambridge, MA)	Flocchini et al. (1981); John et al. (1983); Cahill et al. (1990)	Selective Filtration	2 to 3; --	10	None	Uses large pore (8µm) etched in polycarbonate filters.
BGI-4 (BGI Inc., Waltham, MA)	Blackman and Lippmann (1974); Hering (1995)	Cyclonic Flow	4; --	2.3	None	Generally used in personal sampling applications.
MSA (Mine Safety Appliances Co., Pittsburgh, PA)	Blackman and Lippmann (1974); Hering (1995)	Cyclonic Flow	3.5; --	2	None	Generally used in personal sampling applications.

Sensidyne Model BDX 99R (Sensidyne Inc., Clearwater, FL)	Blackman and Lippman (1974); Hering (1995)	Cyclonic Flow	3.5; --	1.7	None	Also known as Dorr-Oliver design. Generally used in personal sampling applications.
SKC Cat. No. 225-01-02 (SKC Inc., Eighty Four, PA)	Blackman and Lippman (1974); Hering (1995)	Cyclonic Flow	5; --	1.9	None	Generally used in personal sampling applications.
MST Low Flow Rate Sharp Cut Impactor (Harvard Impactor) (Air Diagnostic and Engineering, Harrison, ME)	Marple et al. (1987)	Direct Impactor	2.5; 1.02[d] 10; 1.11[d]	4, 10, 20 4,10	None None	Oiled aluminum impactor plate needs to be replaced after every 24 hours of sampling. Designed for use in indoor air pollution health studies.

a. See Table 4-5 for Federal Register citation and notice date.
b. Sierra-Andersen, Atlanta, GA.
c. General Metal Works, Atlanta, GA.
d. Slope = $\sqrt{d_{16}/d_{84}}$, as defined in text.
e. Slope is estimated based on $\sqrt{d_{10}/d_{90}}$.
f. Inlet for Modules A, B, and C of IMPROVE samplers.

4.5 Filtration Sampling

Introduction

Filtration sampling, which is actually a combination of filtration/impaction sampling, is the most widely used approach for the collection of atmospheric particulates. Filter-based sampling methods are widely used since filters are relatively low in cost, easily stored, and used for subsequent simple and/or complex analyses of collected PM.

Filters capture particles from an air stream by a number of different mechanisms. These mechanisms include inertial impaction, direct interception, diffusional deposition, electrical attraction, and gravitational attraction. The predominant mechanism depends on the flow rate, the composition and nature of the particles, particle size, and the type of filter media.

Topics to be discussed in this section include the basic advantages and disadvantages of air sampling with filters, filtration theory, and some of the criteria necessary for the selection of a filter medium to be used in a specific sampling program. Although the term "filter media" can be extended to cover a large number of media, such as glass fiber, quartz fiber, Teflon®, filter thimbles, and granular beds, this discussion will be confined to the more common media used for particulate matter sampling.

General Considerations

Advantages

Filter sampling for particulate matter has several advantages over other methods. A primary one is the feasibility of handling large volume rates of flow. Some dust sampling instruments, such as midget impingers and thermal precipitators, do not have this capability for large flow rates. Also, after collection, the filtered sample is usually readily available for direct observation.

The number of sizes of filters available has proved to be another advantage. By changing the size of the filter media, the volume of air samples can be varied while maintaining the same linear flow rate through the filter. The selection of sizes also allows filter borders to be designed for use in a variety of situations. This is a definite advantage when the sampling space confines limit accessibility. The variability among filters extends beyond the matter of size alone. Appropriate filters can be obtained that are capable of sampling a wide range of environmental conditions of temperature, humidity, and dust loadings. Further, filters can be found that are adaptable to analysis schemes ranging from microscopic examination to elaborate chemical separation schemes.

Disadvantages

The use of filter media for sampling is not without its difficulties. One disadvantage is related to the variation in physical and chemical properties of filters in any given filter type. In the case of an impaction instrument, once its operating characteristics have been determined, these should remain relatively fixed. On the other hand, in sampling with filters, the media is changed between each sample collection. Although filters that minimize the variability between individual filters of a specific type can be obtained, it is more common to find some differences in performance, particularly between different lots of filters.

Another case in which filters are at a disadvantage is in conjunction with selective particle sizing. A cascade impactor can be designed so that particles of different size ranges can be collected on different stages of the impactor. Such a size separation cannot be done with filter media, although some gradations are possible.

The Theory of Filtration

The most common misconception about air filtration is that it is primarily a sieving mechanism. If this were the case, only particles larger than the pore size would be trapped and the theory of collection would be relatively simple. Actually, except for the kitchen strainer, very few media could be classified as pure mechanical strainers. In air filtration, a number of mechanisms contribute to the collection of particulate matter. The degree to which each one contributes is a function of a number of parameters, discussed below. For a more complete discussion of filtration theory, see R. D. Cadle's book, *The Measurement of Airborne Particulates* (Wiley-Interscience, 1975).

Diffusion

Diffusion is defined as the irregular movement of particles suspended in a fluid, where the fluid is ambient air. The collection of particles on a filter by diffusion depends on a particle concentration gradient between the filter and the air passing between the fibers. The highly concentrated particles in the air stream diffuse to the filter fiber where the concentration is near zero. The diffusion theory further postulates that when the particle comes in contact with the filter, it remains there. The contribution made by diffusion depends on the transit time of particles through the filter, with a longer time resulting in greater diffusion contribution. The amount of diffusion will then depend on linear rate of flow, filter thickness, size of particle, inter-fiber distance, and particle concentration in the air.

Direct Interception

Direct interception is the part of the filter collection mechanism that is analogous to mechanical straining. The interception mechanism takes place when a particle following its air movement streamline comes within a distance from the filter material which is equal to, or less than, the particle radius, so that it comes in contact with the filter medium. As with simple straining, this type of collection predominates where the particles are greater in diameter than the inter-fiber distance, or pore size. The effectiveness of direct interception increases with increasing particle size.

Inertial Collection

As a particle is carried by an air stream, it possesses a certain amount of inertia, depending on its mass and velocity. When a sufficient inertial force has been established, the particle will, as the air stream turns, leave its streamline and continue on its previous path. If the inertia of a particle causes it to strike a filter fiber during the passage of the air stream around the fiber, the particle will be collected. The mechanism of inertial collection plays a major part where high linear velocities of airflow are present. Increasing the particle size and decreasing the fiber diameter (or pore diameter) improves the effect of inertial collection.

Electrical Force

If the aerosol particle has an electrical charge, and the filter fiber has a charge of opposite sign, the particle will be attracted to the filter media. Many investigators believe that such a mechanism has a part to play in the filter sampling of air. Experiments have indicated that both atmospheric particles and filter media possess electrical charges, and that collection does occur by this means. The magnitude of the effect is not well known, but it probably does contribute to the process of collecting particles smaller than the pore size.

Combined Factors

During actual filtration, all four of the above-mentioned collection mechanisms are working together so that it is often difficult to separate one from another. Furthermore, other mechanisms occur that complicate the situation. All four of the methods of collection that have been discussed postulate that once a particle touches the filter material, it stays there. This is not entirely so — there is some reentrainment of particles resulting from the airflow through the filter, picking up and carrying material that has been previously deposited some distance before the particles are once more entrapped by the filter fibers. Increasing the filter face velocity (the velocity across the face or surface of the filter) will increase the chances of reentrainment. All of the above mentioned collection mechanisms result in the accumulation of PM on the filter.

Collection Efficiency of Filters

In the sampling of air particulate matter by filtration, not all particles in the air are collected. That is to say, the collection mechanisms that have been discussed are not 100% efficient. It is, therefore, not sufficient just to know what volume of air was passed through the filter. The fraction of the airborne particles collected must also be known. Collection efficiency may be stated in terms of several parameters. The most common is to determine the *percent penetration* (percent passing through the filter) of a certain particle size as a function of the linear velocity (volume rate of flow divided by the filter area) through the filter. Another way of presenting the efficiency would be to have *percent collection* of a certain particle size as a function of linear velocity through the filter. Percent penetration and percent collection efficiencies are useful in laboratory settings with known particle size distributions; however, they are difficult to use for ambient air since particle size distribution information is rarely known outdoors.

There is one other type of filter collection efficiency reported in literature. This is a *mass collection efficiency* based entirely on the percentage of the mass of the airborne particles that is collected. This can be grossly misleading because the small particles predominate in number, and yet, constitute a minor fraction of the total particulate matter mass. The only time a mass collection efficiency would represent a total particle collection efficiency would be if all the particles were of the same size.

Theory of Collection Efficiency
Before continuing the discussion of collection efficiency, it is necessary to discuss the theory of collection efficiency for the various collection mechanisms previously mentioned, and also, the effect of various parameters on collection. Figure 4-26 shows a qualitative picture of the theoretical percent penetration versus linear velocity that might be expected for a given filter and an aerosol with a specific size particle. By referring to this graph, and the associated notes, the interrelation of the various mechanisms can be examined.

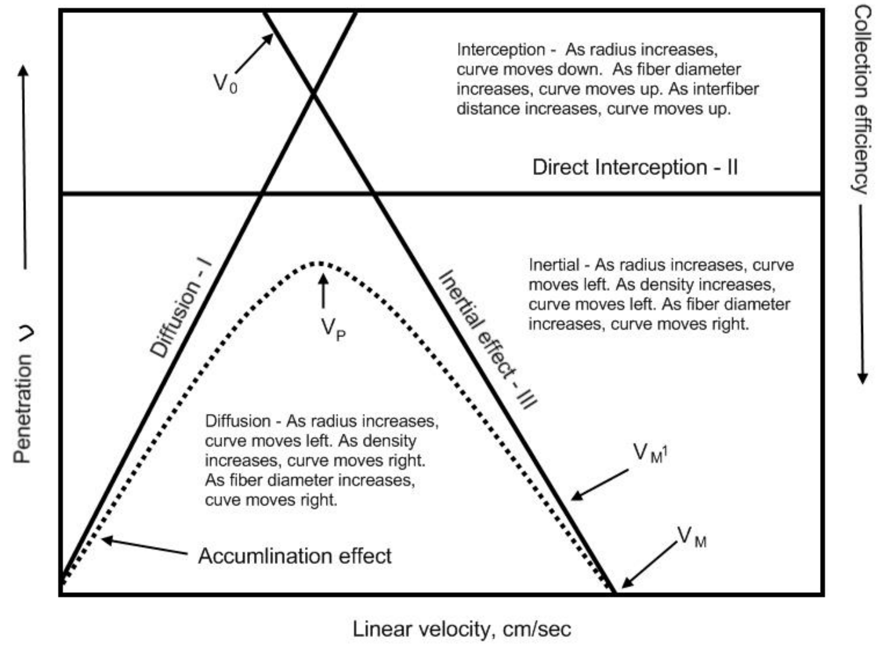

Figure 4-26. Filtration mechanisms.

Diffusion Efficiency. The diffusion line I of Figure 4-26 shows how the diffusion mechanism is affected by linear velocity. As the velocity increases, the diffusion mechanism decreases. As previously mentioned, this is due to the shorter transit time through the filter at the higher flow rates. The diffusion function always passes through the origin, but the slope varies with the particle radius, the filter fiber diameter, and the distance between filter fibers.

As the particle radius increases, the slope becomes greater, thus resulting in a reduced diffusion effect for a given linear velocity. This is because larger particles are not as readily affected by diffusion mechanisms as are smaller particles.

The effects of fiber diameter and inter-fiber distance are quite similar. As either of these two parameters increases, the influence of the diffusional mechanism increases and the slope of the line decreases. A greater fiber diameter increases the diffusion effect because, for a given linear velocity, the particle spends a longer time passing by a filter fiber. The effect of inter-fiber distance is similar, as it too affects the transit time of the particle by a filter fiber. The greater the open space in the filter is, the larger the inter-fiber distance. Therefore, for a given overall linear velocity, the velocity in the open space of the filter is less for larger inter-fiber distance, and transit time is longer.

Direct Interception Efficiency. As previously mentioned, direct interception is analogous to simple mechanical straining. Direct interception is shown in line II of Figure 4-26. It shows that there would not be any effect by changing linear velocity on this collection mechanism.

The effects of the particle radius and inter-fiber distance on the interception mechanism are quite simple. As the particle radius increases, the percent penetration decreases, as would be expected for straining. As inter-fiber distance increases, the percent penetration increases for a mechanical straining.

The relation between particle penetration and fiber diameter for interception is somewhat more involved. As the fiber diameter increases in size, the air flowlines are affected at an increasing distance upstream from the fiber. This may cause some of the flowlines to diverge from a path that would have brought the particle within contact distance of the fiber. Therefore, as the fiber diameter increases, the collection efficiency due to interception decreases.

Inertial Effect Efficiency. The inertial collection of particles depends on the particles leaving their air flowlines and contacting a filter fiber due to their inertial forces. For a particle of a given size, this effect would start to show at some velocity, V_P, and would reach a maximum at some greater velocity, V_M. The fact that the effect increases with velocity is due to the dependence of inertial forces on both mass and velocity. Although Figure 4-26, line III, shows a zero percent penetration for this mechanism at V_M, the penetration might be significant, depending on the inter-fiber distance. If a larger inter-fiber distance existed, the maximum effect might occur at some point V_{M1}, in which case a definite amount of penetration would occur.

The effect of increasing particle radius in inertial collection is improved collection for a given linear velocity. This is related to the fact that the larger the particle, the greater the probability of it coming within a distance from the filter fiber where it will make contact. Table 4-2 lists the collection efficiency of some filter media as a function of particle size.

The effect of increasing particle density also improves inertial collection. Like the effect of velocity, this is due to the increase of inertial forces, thus causing greater deviation from the air flowlines.

As the filter fiber diameter increases, the effect of inertial collection decreases. With the air flowlines being affected at a greater distance upstream from the fiber, the change in their trajectory is much more gradual and, therefore, the tendency of inertial forces to cause a particle to leave a flowline is less.

Table 4-2. Collection efficiency of commonly used filter types for particles > 0.3 µm diameter. Measurements made via Royco particle counter.[a]

Collection Efficiency (%) for Commonly Used Filter Types										
	Particle Size (µm) in equivalent diameters									
Filter	**Size (mm)**	**No. of trials**	**0.32**	**0.4**	**0.5**	**0.64**	**0.8**	**1.0**	**1.3**	**1.6**
0.8 µ Nucleopore	47	1	82	96	99	99	100	100	100	100
5.0 µ Nucleopore	90	1	83	95	98	97	98	100	100	100
3.0 µ MF millipore (SS)	90	3	99.93	99.98	100	100	100	100	100	100
5.0 µ MF millipore (SM)	47	1	100	100	100	100	100	100	100	100
5.0 µ MF millipore (SM)	90	1	100	100	100	100	100	100	100	100
5.0 µ Teflon® millipore (LS)	90	1	99	99.6	100	100	100	100	100	100
8.0 µ MF millipore (SC)	47	1	96	99	99	99	96	99	100	—
10 µ Teflon® millipore (LC)	90	1	96	99	99	99	100	100	100	100
1.2 µ Silver membrane	47	2	99.9	100	100	100	100	100	100	100
S&S 0.45 (B6A) cellulose acetate	47	1	100	100	100	100	100	100	100	100
Gelman GA-1 cellulose acetate	47	1	99	100	100	100	100	100	100	100
Glass fiber filters										
Gelman A	47	2	99.8	99.8	99.6	99.7	99.1	99	99	97
Gelman A	25	1	100	100	100	100	100	100	100	100
Gelman A acid washed	25	1	99.9	100	100	100	100	100	100	100
Reeves angel # 900 AF	47	1	99.9	100	99.9	100	100	100	100	100
MSA 1106 BH	47	1	100	100	100	100	100	100	100	100
S&S #25 acid washed	47	3	26	53	65	64	69	71	79	88
TFA[b]	47	2	38	67	80	81	83	85	84	87
Whatman 41	47	1	63	83	90	84	89	81	94	100
S&S green ribbon #559	47	1	69	84	88	87	93	98	97	100

a. Face velocity in cm/sec for 25-, 47-, and 90-mm filters is 0.82, 0.31, and 0.11, respectively.

b. After sampling 500 ft^3 of room air, the filtration efficiency of TFA increased to 90% for 0.3 µm particles with other values in the range of 80 to 90% for sizes up to 1.6 µm. This efficiency was not significantly altered by discharging the filter over a radioactive source.

Overall Efficiency. In filter sampling, all of the collection mechanisms are taking place simultaneously and their effects are algebraically additive. The overall relation between percent penetration and linear velocity might well look like the dotted line in Figure 4-26.

From this overall efficiency curve, there appears to be some velocity, V_P, where a maximum penetration occurs. It should be pointed out, however, that if the direct interception effect is dominant enough, the overall efficiency curve may well have a flat plateau, rather than a single velocity of maximum penetration.

The mechanism of electrical forces has not been covered in this discussion of the theory of collection efficiency. The degree to which it will change the overall efficiency is dependent on many factors. The theoretical aspect of this effect is beyond the scope of this discussion, but it may play an important part in overall efficiency in certain instances.

Experimental Collection Efficiencies

Several investigators have studied the actual collection efficiencies of filter media, and their results are reported in the literature (ACGIH 1985, Caroff 1973, Liu 1978, Ramskill 1951). A degree of caution must be exercised in utilizing this experimental data. A number of different types of particulate matter have been used, including dioctyl phthalate (DOP) smoke, atmospheric dust, duraluminum dust, radon daughter products, polystyrene aerosols, and lead fumes. The experimental results of the various investigators often appear to be in great disagreement for many of the filter media, and these differences should be evaluated in selecting an efficiency value to use.

One additional complicating factor should be mentioned in relation to filter efficiency. During the time that the sampler is running, the increasing amount of particles that accumulate on the filter will cause the collection efficiency to improve as sampling continues. This is due to the adherence of particles on previously collected particles, commonly known as the filter cake effect. As this occurs, however, filter cake thicknesses that are too large can increase the resistance of the filter and thus decrease the collection efficiency. The decreased collection efficiency for large cake thicknesses can result from clogging the filter, particle bounce, and other escape mechanisms. When the filter cake is too thick, the high resistance across the filter can lead to a reduced flow rate. Most pumps currently used at monitoring locations are able to compensate for typical sample loading resistances (i.e., pressure drop associated with the buildup of the filter cake), and thus maintain desired flow rate.

Characteristics of Filter Media

A great number of individual types of filter papers are available. For particulate matter sampling, in general, they fall into four main categories: cellulose fiber, glass fiber, mixed fiber, and membrane filters. These various categories will be discussed in terms of their general characteristics, sampling considerations, and analysis considerations. (See Table 4-7 at the end of the section.)

Cellulose Fiber Filters

The filter papers in this category are typically called chemical filters. They were designed for use in "wet" chemistry where liquid-solid separations were desired. Although not designed with air sampling in mind, a number of these filters have seen extensive application in this area (see Table 4-3).

Table 4-3. Cellulose fiber filters.

Filter	Void size (microns)	Fiber diameter (microns)	Thickness (microns)	Weight per unit area (mg/cm^2)	Ash content (%)	Maximum operating temp. (°C)	Tensile strength	Flow resistance 100 ft/min (in. H_20)
Whatman							1.67 kg/cm	
1	2+	—	130	8.7	0.06	150		40.5
4	4+	—	180	9.2	0.06	150		11.5
32	1-	—	150	10.0	0.025	150		38 (1 fm)
40	2	—	150	9.5	0.01	150		54
41	4+	—	180	9.1	0.01	150	1.41 kg/cm	8.1
42	>1	—	180	10.0	0.01	150		46 (28 1 fm)
44	>1	—	150	8.0	0.01	150		40 (28 1 fm)
50	1	—	100	10.0	0.025	150		49 (28 1 fm)
541	4+	—	130	8.2	0.008	150	2.24 kg/cm	—
S&S 604	—	—	200	—	0.03	80		8.5
MSA Type S	—	—	100.0		1.3	120		6.5
Cellulose	—	—	1000		1.3	120		
Corrugated	—	—						
Cellulose	—	—	1000		1.3	120		
MSA BM-2133			1830	32.7	0.12		0.58 kg/cm	9.1
IPC 1478	—	Av. 17	560-760	14.6	0.04	120	0.18 kg/cm	0.31
Gelman W-41	24							

Sampling Considerations. Cellulose fiber filters are made of purified cellulose pulp, which can easily ignite, thus rendering them ineffective at high operating temperatures. The low ash content of these filters makes them highly suitable to analysis where heat or chemical ashing is a required preparation. These filters generally have a high affinity for moisture. This limitation means that the relative humidity must be controlled while weighing the filters to ensure there is no error introduced by absorbed moisture. Recent studies show that cellulose filters irreversibly absorb water; thus, a control blank is required when humidity is a problem. Cellulose filters also enhance the artifact formation of sulfate and nitrate.

Specific Filters. Whatman 41 filter paper is the most widely used of the cellulose fiber filters. Whatman 41 has become the preferred substitute for glass fiber filters for high-volume sampling, because of its good collection efficiency and acceptability for further chemical analyses. It has also received wide use in all types of metals analysis, including neutron activation analysis, because of the low blanks or background levels of metals on the clean filters. This filter has also found applications as the tape used with paper tape samplers for the determination of soiling index.

The Mine Safety Appliances (MSA) type "S" filter is well adapted to high-volume sampling because of the low pressure drop associated with this technique. This filter is difficult to handle because of its bulkiness, and its variable ash content and organic binder make it unsuitable for some chemical analyses.

TFA filters have also been used for high-volume sampling when extensive chemical analysis is required. Whatman 41 is preferred over this filter because of the higher collection efficiency (see Table 4-2).

Glass Fiber Filters

These filter papers are made from finely spun glass fiber by combining the fiber with an organic binder and compressing this material in a paper machine. These filters have seen increasing use in air sampling.

Sampling Considerations. Glass fiber filters have the ability to withstand high temperatures (up to 540°C), thus making them most attractive for stack sampling. Quartz fiber filters, a subset of glass fiber filters, are able to withstand up to 1000°C. Consequently, quartz fiber filters are used in speciation samplers (discussed in Chapter 5) for the quantification of carbon by thermal-optical methods. Glass fiber filters are further typified by high collection efficiency. In some cases, the organic binder may interfere with subsequent analysis, so the filter is flash-fired to remove the binder material. This causes some loss in tensile strength and usually requires that a backing material be used during sampling. The glass filters are non-hygroscopic, thus allowing them to be used in areas where humidity is high. Being glass also makes them the filter choice for most corrosive atmospheres. All of the filters in this category are quite fragile and must be handled with care.

Analysis Considerations. Glass fiber filters, because of the high silicate content, are extremely difficult to ash by chemicals or heat. Therefore, extraction procedures are performed on these filters to remove the sample for subsequent chemical analysis. Overall, flash-fired glass fiber filters, because they are non-hygroscopic, can be used in corrosive atmospheres and are free of organic binders that are widely used for ambient air sampling.

The pH of the filter will affect the collection of the sample. It has been recommended that neutral pH ($6.5 < \mathrm{pH} < 7.5$) filters be used because there is less absorption of acid gases onto the filter. Significantly different results can be obtained when sampling side-by-side with filters of different pH values.

Specific Filters. The MSA 1106 BH is one of the flash-fired glass fiber filters and, therefore, is free of organic binder. The Gelman Spectro Grade Type A Glass Fiber Filter is a neutral pH glass fiber filter rated as ultra-pure for metals analysis to minimize interference with trace metal background values. (Each box of 8- by 10-inch filters contains assay information on trace metals for the enclosed filters.) Spectro grade filters do not absorb detectable amounts of SO_2 from the atmosphere, thereby minimizing its effect. A summary of the physical characteristics of some commonly-used glass fiber filters is given in Table 4-4.

Mixed Fiber Filters

These filters possess the characteristics of the individual fibers composing them. The chemical analysis of mixed fiber filters also depends on the individual fiber constituents. General characteristics of a number of the members of this category are given in Table 4-5.

Table 4-4. Glass fiber filter characteristics.

Filter	Void size (microns)	Fiber diameter (microns)	Thickness (microns)	Weight per unit area (mg/cm^2)	Ash content (%)	Maximum operating temp. (°C)	Tensile strength	Flow resistance 100 ft/min (in. H_20)	Benzene extract/ 100 in.^{2} (mg)
MSA									
1106B[*]			180-270	6.1	- 95	540	3.5 lb/in.	19.8	17.3
1106BH[#]			180-460	5.8	- 100	540	1.5 lb/in.	19.8	0.6
									0.6
Gelman									
A[#]			380	9.3	99.4	480		18.9	
E[*]			380	10.0	98.1	480		18.9	
G			810	11.6		480		3.0	
M			580	10.8		480		6.1	
H			510	12.7		480		21.7	
Whatman									
AGF/A[#]	>1		340	5.3	100	540	1.29 lb/in.		0.8
AGF/B[#]	>1		840	15.0	100	540	3.14 lb/in.		3.2
AGF/D	>1		460	5.5	100	540	0.56 lb/in.	2.3@2 1fm	
AGF/E	>1		890	15.0	100	540	1.07 lb/in.		
AGF/F	>1		380	6.3	100	540	0.73 lb/in.		
H&V									
H≅93		0.6	460-560	9.3	96-99	540	2.5 lb/in.		
H≅94		0.5≅3	380	8.2	96-99	480	2.5 lb/in.		
S&S									
24[*]									
26[#]			200	6.05					0.3
27[*]			125-180		98	400			
29[#]			127	5.4	98	400			0.6

[#] without organic binder

[*] with organic binder

Table 4-5. Mixed fiber filter characteristics.

Filter designation	Composition	Void size (microns)	Fiber diameter (microns)	Thickness (microns)	Weight per unit area (mg/cm^2)	Ash content (%)	Maximum operating temp. (°C)	Tensile strength	Flow resistance at 100 ft/min [~50 cm/sec] (in. H$_2$0)
H&V H≅70, 9 mil	Cellulose asbestos		0.1-35	230	8.2	20-25	150	2.5 lb/in.	17
H≅70, 18 mil	Cellulose asbestos		0.1-35	460	15.4	20-25	150	4.0 lb/in.	26
H≅64	Cellulose asbestos		0.1-35	830-1090	22.7	15-20	150	2.0 lb/in.	15
H≅90	Cellulose glass		9-35	685	13.4	70	150	3.2 lb/in.	0.4
H≅91	Cellulose glass		1.5-35	710	13.5	80	150	3.5 lb/in.	0.89
N≅15	Synthetic fiber & glass		0.5-15	1270	24.9	15	150	1.0 lb/in.	9.9
5≅G	Synthetic fiberglass & cotton		0.5-15	685	14.5	4-6	150	gauze backed	2.0
MSA glass & cellulose	Glass & cellulose			1000			120		
Whatman ACG/A	Glass & cellulose	>1		330	5.5		150	270 gm/cm	0.9 (20 1 fm)
ACG/B	Glass & cellulose	>1		990	19.5		150	330 gm/cm	2.6 (20 1 fm)
H&V CWS≅6	Cellulose asbestos			762		11%			17
H&V AEC≅1	Cellulose asbestos			762		13%			13.3
VM≅100 Gelman	Vinyl metracel	10.0							
VM≅1	Vinyl metracel	5.0							

Membrane Filters

This filter media consists of dry gels of cellulose esters, usually produced as cellulose acetate or cellulose nitrate, polyvinyl chloride, acrylonitrile, and Teflon®. The filters are cast on a smooth, flat substrate and exposed to a controlled atmosphere. This process can control both the internal membrane structure and pore size. Some filters are formed with pores while others are formed as sheets with pores formed later.

Sampling Considerations. Membrane filters are typically very brittle and require careful handling. In air sampling, they should be backed by some support structure to avoid breakage. The filters are not well suited to sampling at elevated temperatures, as they have an operating temperature range comparable to cellulose fiber filters (see Table 4-6).

The particle size collected by membrane filters has been found to be much smaller than the pore size; this is thought to be due to electrostatic forces.

Membrane filters have appreciable pressure drops, and this may limit the volume of air that can be sampled. Another factor limiting the volume of air that can be sampled is the build-up of a second layer of dust on the filter surface. This layer has a tendency to slough off, causing loss of part of the sample.

Analysis Consideration. One advantage of membrane filters is that they are primarily surface collectors and are not prone to absorption interferences when analyzed under spectrometric methods. The membrane filters lend themselves very readily to particle size analysis by microscopy. By using an immersion oil with an index of refraction (N_D) equal to that of the filter, the filter can be made transparent to light, thus allowing light-transmitted microscopic analysis. However, care must be taken to ensure that the N_D of the particle is not the same as the N_D of the immersion oil.

Membrane filters can also be readily ashed and leave very little residue. This can be a definite advantage in some analysis schemes. Most membrane filters are also readily soluble in many organic solvents, thus allowing removal of particulate matter with little problem.

Commonly Used Filter Media for Particulate Sampling and Analysis

The 1997 draft "EPA Guideline on Speciated Particulate Monitoring" (Chow 1997) includes a discussion on the commonly used filter media for particulate sampling and analysis, including $PM_{2.5}$ and PM_{10}. A summary table taken from this reference, presenting filter type, filter size, physical characteristics, chemical characteristics, and compatible analysis methods is included here as Table 4-7.

Table 4-6. Membrane filter media.

Filter	Pore size (microns)	Index refraction	Thickness (microns)	Weight per unit area (mg/cm^3)	Ash content (%)	Maximum operating temp. (°C)	Tensile strength	Flow resistance, 100 ft/min (in. H_2O)
Millipore SM	5.0	1.495	170	3.6	0.0001	125	100 psi	19
SS	3.0	1.495	170	3.8	0.0001	125	150 psi	38
WS	3.0		150	4.9	″	″		-100
RA	1.2	1.512	150	4.2	″	″	300 psi	62
AA	0.80	1.510	150	4.7	″	″	350 psi	91 (39)*
DA	0.67	1.510	150	4.8	″	″	400 psi	120
HA	0.45	1.510	150	4.9	″	″	450 psi	210
WH	0.45		150	5.7	0.0001	″		-270
							0.41 kg/cm^2	11
Gelman AM≅1	5.0		200	3.6		″	0.72 kg/cm^2	33
AM≅3	2.0		200	6.6		″		73
AM≅4	0.65		200			″		
AM≅5	0.65		200			″		
AM≅6	0.40		200	5.8		″		
S&S	7.5		180-250	6.3-8.7	0.01	Continuous		
AF≅600						100		
AF≅400	4.0		180-250	6.3-8.7	0.01	Peak 200		
AF≅250	2.0		160-210	5.6-7.3	0.008	″		
AF≅150	0.85		160-210	5.6-7.3	0.008	″		
AF≅100	0.70		Av-150	Av 5.3	0.007	″		
AF≅50	0.60		Av-135	Av 4.7	0.006	″		
AF≅30	0.40		Av-120	Av 4.2	0.005	″		
Gelman GM≅1	5.0	1.49				Dry 176		
GM≅3	1.2	1.49				176		
GM≅4	0.80	1.49				176		
GM≅6	0.45	1.49				176		
GM≅8	0.20	1.49				176		
GM≅9	0.10	1.49				176		
GM≅10	0.05	1.49				176		

*Alternate value reported.

Table 4-7. Commonly used filter media for particulate sampling and analysis.

Filter Type, (Major Manufacturer, and Catalog No. or Trade Name)	Filter Size	Physical Characteristics	Chemical Characteristics	Compatible Analysis Methods[a]	No. of Filters per Box
Ringed Teflon®-membrane (Gelman Scientific; Ann Arbor, MI; Teflon® R2PJ047, R2PJ037)	25 mm 37 mm 47 mm	Thin membrane stretched between polymethlypentane ring. White surface, nearly transparent. Minimal diffusion of transmitted light. High particle collection efficiencies. Cannot be accurately sectioned. 1.2, 2.0, 3.0, 5.0 and 10μm pore sizes (determined from liquid filtration). Melts at ~60°C. High flow resistance.	Usually low blank levels, but several contaminated batches have been found. Made of carbon-based material, so inappropriate for carbon analysis. Inert to adsorption of gases. Low hygroscopicity. Low blank weight.	Gravimetry, OA, XFR, PIXE, INAA, AAS, ICP/AES, ICP/MS, IC, AC	50 50 50
Ringed Teflon®-membrane (Pallflex, Putnam, CT)	25 mm 37 mm 47 mm	Thin film of Teflon® attached to polyolefin ring without adhesive.	Made of carbon-based material, so inappropriate for carbon analysis. Inert to adsorption of gases. Low hygroscopicity. Low blank weight.	Gravimetry, OA, XRF, PIXE, INAA, AAS, ICP/AES, ICP/MS, IC, AC	25 25
Backed Teflon® membrane, (Gelman Scientific, Ann Arbor, MI; "Zeflour"; 2μm, P5PJ037 or P5PJ047; 1μm, P5PL037 or P5PL047)	37 mm 47 mm 20.3 × 25.4cm	Thin membrane mounted on thick polypropylene backing. White opaque surface, diffuses transmitted light. High particle collection efficiencies. Melts at ~60°C. High flow resistance. 1 μm and 2 μm pore sizes.	Usually low blank levels. Made of carbon-based material, so inappropriate for carbon analysis. Inert to adsorption of gases. Higher background levels for XRF and PIXE than Teflon® owing to greater filter thickness. Low hygroscopicity. High blank weight.	Gravimetry, XRF, PIXE, INAA, AAS, ICP/AES, ICP/MS, IC, AC	50 50 25

Backed Teflon® membrane, (Pallflex, Putnam, CT)	25 mm 37 mm 47 mm	TFE porous membrane on TFE support. Smooth surface. 0.30 µm @ 99% efficiency.	Neutral pH. Usually low blank levels. Made of carbon-based material, so inappropriate for carbon analysis. Inert to adsorption of gases. Higher background levels for XRF and PIXE than Teflon®, due to greater filter thickness. Low hygroscopicity. High blank weight. Retains average tare weight of 7.6 grams.	Gravimetry, XRF, PIXE, INAA, AAS, ICP/AES, ICP/MS, IC, AC	50 50
Nylon membrane, (Gelman Scientific, Ann Arbor, MI: "Nylasorb", #66509)	47 mm 90 mm	Thin membrane of pure nylon. White opaque surface, diffuses transmitted light. 1µm pore size. Melts at ~60°C. High flow resistance.	High HNO_3 collection efficiency. Passively adsorbs low levels of NO, NO_2, PAN, and SO_2. Low hygroscopicity. Low blank weight.	IC, AC	100 50
Silver membrane (Millipore Corp., Marlborough, MA)	25 mm[b] 37 mm[c]	Thin membrane of sintering, uniform metallic silver particles. Grayish-white surface diffuses transmitted light. Melts at ~350°C. High flow resistance.	Resistant to chemical attack by all fluids. Passively adsorbs organic vapors. Low hygroscopicity. High blank weight.	Gravimetry, XRD	50 25
Cellulose esters membrane (Millipore Corp., Marlborough, MA; "Nitrocellulose")	37 mm 47 mm[d]	Thin membrane of cellulose nitrate mixed esters, and cellulose acetate. White opaque surface diffused transmitted light. 0.025, 0.05, 0.1, 0.22, 0.30, 0.45, 0.65, 0.80, 1.2, 3.0, 5.0, and 8.0 µm pore sizes. Melts at ~70°C. High flow resistance.	High hygroscopicity. Negligible ash content. Dissolves in many organic solvents. Low blank weight.	Gravimetry, OM, TEM, SEM, XRD Biomedical applications	100 100

Polyvinyl Chloride membrane (Millipore Corp., Marlborough, MA)	25 mm 37 mm 47 mm	Hospital-grade polyvinyl chloride membrane. White opaque surface, diffuses transmitted light. 0.2, 0.6, 0.8, 2.0, and 5.0 µm pore sizes. Melts at ~50°C. High flow resistance.	Dissolves in some organic solvents. High hygroscopicity. Low blank weight.	XRD	100 100 100
Polycarbonate membrane, (Corning CoStar, [formerly Nuclepore Corp.], Cambridge, MA; #111129) (Poretics, Minnetonka, MN)	25mm 37mm 47mm[b]	Smooth, thin, polycarbonate surface with straight through capillary holes. Used for particle size classification. Light gray surface, nearly transparent. Minimal diffusion of transmitted light. Low particle collection efficiencies, <70% for some larger pore sizes. Retains static charge. 0.1, 0.3, 0.4, 0.6, 1.0, 2.0, 3.0, 5.0, 8.0, 10.0, and 12.0 µm uniform pore sizes. Melts at ~60°C. Moderate flow resistance.	Low blank levels (made of carbon-based material, so inappropriate for carbon analysis). Low hygroscopicity. Low blank weight.	Gravimetry, OA, OM, SEM, XRF, PIXE	100 100 100
Pure quartz-fiber (Pallflex Corp., Putnam, CT; 2500 QAT-UP)	25 mm 37 mm 47 mm 20.3 × 25.4 cm	Mat of pure quartz fibers. White opaque surface, diffuses transmitted light. High particle collection efficiencies. Soft and friable edges flake in most filter holders. Melts at >900°C. Moderate flow resistance.	Pre-washed during manufacture - low blank levels for ion. Contains large and variable quantities of Al and Si. Some batches contain other metals. Passively adsorbs organic vapors. Adsorbs little HNO_3, NO_2, and SO_2. Low hygroscopicity.	ICP/AES, ICP/MS, IC, AC, T, TOR, TMO, TOT, OA	100 25 25 25

Mixed quartz-fiber (Whatman Corp., Hillsboro, OR; QM/A #1861865)	37 mm 47 mm 20.3 × 25.4 cm	Quartz (SiO_2) fibers with ~5% borosilicate content. White opaque surface, diffuses transmitted light. High particle collection efficiencies. Some batches can melt at ~500°c. Effects on thermal carbon analysis are unknown. Becomes brittle when heated. Low flow resistance.	High blank weight. Contains large and variable quantities of Na, Al, and Si in all batches. Variable levels of other metals are found in many batches. Passively adsorbs organic vapors. Adsorbs little HNO_3, NO_2, and SO_2. Low hygroscopicity. High blank weight.	Gravimetry, XRF, PIXE, AA, ICP/AES, ICP/MS for some metals, IC, AC, T, TOR, TMO, TOT	100 100 25
Cellulose-fiber 41 (Whatman Corp., Hillsboro, OR; #1441047)	25 mm 47 mm	Thick mat of cellulose fibers, often called a "paper" filter. White opaque surface, diffuses transmitted light. Low particle collection efficiencies, <70% for some variations of this filter. High mechanical strength. Burns at elevated temperatures (~150°C, exact temperature depends on nature of particle deposit). Variable flow resistance.	High purity, low blank levels. Made of carbon-based material, so inappropriate for carbon analysis. Adsorbs gases, especially water vapor. Most appropriate for adsorbing gases such as HNO_3, SO_2, NH_3, and NO_2 when impregnated with reactive chemicals. High hygroscopicity. High blank weight.	Gravimetry, XRF, PIXE, INAA, AAS, ICP/AES, ICP/MS, IC, AC	100 100
Cellulose-fiber 31ET (Whatman Corp., Hillsboro, OR; #3031F915	47 mm 46×47 cm		High purity, low blank levels. Made of carbon-based material, so inappropriate for carbon analysis. Adsorbs gases, especially water vapor. Most appropriate for adsorbing gases such as HNO_3, SO_2, NH_3, and NO_2 when impregnated with reactive chemicals. High hygroscopicity. High blank weight.	Gravimetry, XRF, PIXE, INAA, AAS, ICP/AES, ICP/MS, IC, AC	100 25

Teflon®-coated glass-fiber (Pallflex, Putnam, CT; TX40H120)	37 mm 47 mm	Thick mat of borosilicate glass fiber with a layer of Teflon® on the surface. Glass fiber supporting Teflon® is shiny. High particle collection efficiencies. Glass melts at ~500°C. Teflon® melts at ~60°C. Low flow resistance.	Low blank levels for ions (glass backing and carbon content make it less suitable for elemental and carbon analyses). Inert to adsorption of HNO_3, NO_2, and SO_2. Low hygroscopicity. High blank weight.	Gravimetry, IC, AC	100 100
Glass fiber (Gelman Scientific, Ann Arbor, MI; Type A/E)	25 mm 47 mm 20.3 × 25.4 cm (available in 13 mm to 293 mm sizes)	Borosilicate glass fiber. White opaque surface, diffuses transmitted light. High particle collection efficiencies. Melts at ~500°C. Low flow resistance.	High blank levels. Adsorbs HNO_3, NO_2, SO_2, and organic vapors. Low hygroscopicity. High blank weight.	Gravimetry, OA, XRF, PIXE, INAA, AAS, ICP/AES, IC, AC	500 100 100

a AAS = Atomic Absorption Spectrophotometry
AC = Automated Colorimetry
IC = Ion Chromatography
ICP/AES = Inductively-Coupled Plasma with Atomic Emission Spectrophotometry
ICP/MS = Inductively-Coupled Plasma with Mass Spectrophotometry
INAA = Instrumental Neutron Activation Analysis
OA = Optical Absorption or Light Transmission (b_{abs})
OM = Optical Microscopy
PIXE = Proton-Induced X-Ray Emissions
SEM = Scanning Electron Microscopy
T = Thermal Carbon Analysis
TEM = Transmission Electron Microscopy
TMO = Thermal Manganese Oxidation Carbon Analysis
TOR = Thermal/Optical Reflectance Carbon Analysis
TOT = Thurman Optical Transmission Carbon Analysis
XRD = X-Ray Diffraction
XRF = X-Ray Fluorescence

b Available in 0.45 μm pore size.
c Available in 0.80 μm pore size.
d Filter disc is available in-size between 13 mm to 293 mm, depending on the pore size.
e Available by special order.

Sample Problems

Problem 1: Filter Selection

A filter is to be chosen for subsequent analysis by a chemical ashing technique. The maximum vacuum flow resistance the pump can overcome is about 10 in. of water when the face velocity is about 100 ft/min. When dealing with atmospheric sampling, the temperature is not a limiting factor since most filters will operate at temperatures over 100°C (212°F). Which filter, based on the available information, would be the best choice?

Solution: Tables 4-4 and 4-5 show that glass fiber and mixed fiber filters have relatively high ash contents, making them impractical for chemical ashing. Tables 4-3 and 4-6 show that, generally, cellulose fiber filters and membrane filters exceed the requirements of the pumps. Table 4-3 shows that Whatman 41, S&S 604, MSA BM-2133, and the IPC 1478 all have ash contents less than 1% and flow resistances less than 10 in. H_2O. These would all be acceptable, and availability would determine which would be used.

Problem 2: Filter Selection

The pump capacity from Problem 1 has now been doubled so that 20 in. H_2O at 100 ft/min can now be sampled. An efficiency of 100% for all particles down to 0.3 μm is desired. Which filter should be used?

Solution: According to Table 4-2, the 5.0 μm MF Millipore (SM) 47 mm and 90 mm, S&S B6A cellulose acetate, Gelman A 25 mm, and MSA 1106 BH all show apparent particle efficiencies of 100% for all sizes. According to Table 4-4, both the Gelman and MSA filters show an ash content over 95%, and therefore are not acceptable. The S&S B6A does not appear on Tables 4-3 through 4-6, but since the cellulose acetate is a mixed fiber filter, we can assume the ash content is also too high. According to Table 4-6, the 5.0 μ Millipore SM has a low ash content (0.0001%), an acceptable flow resistance (19 in. H_2O), and is the most acceptable filter.

Problem 3: Filter Extraction

A filter is needed for subsequent analysis by acid extraction. The sampling atmosphere is very humid. The flow resistance must be kept below 10 in. H_2O. Which filter should be used?

Solution: Cellulose filters are very hygroscopic, so they should not be used in this situation. Membrane filters have extremely high flow resistances, so they, too, should not be used in this situation. Glass fiber filters are non-hygroscopic and are the filters of choice in water-vapor laden atmospheres. According to Table 4-4, Gelman G or M filters could be used since they both qualify for the low flow resistance requirements.

Summary

No single type of filter is the right one for all air sampling problems. The choice of filter also depends on the analysis method required for different particulate constituents. In evaluating a filter, one must consider many factors: general filter characteristics, collection efficiency, background filter impurities, sampling conditions, ease of analysis, light absorption characteristics, flow resistance, and the purpose for which the sample is being taken.

4.6 Gravitational Sampling

Gravitational sampling, as briefly discussed here, refers to the amount of precipitation (solid or liquid) which reaches the ground over a stated period of time. The sampling time periods reported for total solids are 24 hours or more, and as much as a 30-day time period. This discussion addresses the use of dustfall buckets or jars for solids, and nonrecording and recording gauges typically used for rainfall.

Dustfall Bucket or Jar

The dustfall bucket had been one of the earliest sampling devices for particulate matter in the atmosphere. Although not widely used by EPA anymore, this method was used extensively in the early days of air monitoring and is still used throughout the world. The bucket or jar was made of resistant material and often placed in a stand to prevent the container from spilling. A wire rim was used to prevent the container from collecting bird droppings. The dustfall bucket is used mostly as a bulk collector for wet (rainwater) and dry (dust) deposition. Results were calculated by filtering the liquid, with subsequent weighing of the remaining solids.

Precipitation Collectors

As reported in EPA's *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume IV-Meteorological Measurements*, EPA/600/R-94/0-38d, revised 1995, the National Weather Bureau Station's precipitation collectors are of two basic types: nonrecording and recording devices. The nonrecording precipitation collector or gauge is constructed of a cylinder, closed at one end and open at the other. The depth of the liquid in the collector is typically measured with a measuring ruler calibrated in subdivisions of centimeters or inches. To improve precipitation resolution as in the case of the standard 8-inch gauge, the collector is constructed to satisfy National Weather Station (NWS) specifications, which require a ratio of 10:1 between the area of the outside collector cylinder and the inside measuring tube. A funnel attached to the gauge directs the precipitation into the collecting tube and minimizes evaporation losses. A specialized nonrecording gauge is available for collecting programs involving the chemical and/or radioactive analysis of precipitation. The collector includes a sensor that detects the start and end of precipitation and automatically releases a lid to open and close the precipitation gauge.

Recording gauges consist of two basic designs based on their operating principles: the weighing-type gauge and the tipping bucket-type gauge. The weighing gauge is known as the Universal gauge because it may be used for liquid and frozen precipitation. This gauge incorporates a chart drum that is made to rotate either by an 8-day spring-wound clock or a battery-powered clock. A quartz crystal mechanism with gear shafts allows for a wide range of rotation periods from 12 hours to 30 days. In the tipping bucket gauge, the balance of the buckets and the leveling of the bucket frame are critical. Power is typically 6V D.C., and the signal is provided by a switch closure each time the bucket tips (0.01 inches of rainfall per bucket). The accuracy of the gauge is given as 1% for rainfall rates of 1 in./hr or less, 4% for rates of 3 in./hr, and 6% for rates up to 6 in./hr.

4.7 Electrostatic Precipitators

These next two sections address the use of electrostatic and thermal precipitators for the collection of particulate matter. Only a brief discussion is included since these techniques are more commonly used in air cleaning applications or special air monitoring research projects than for routine use in ambient air sampling. The following discussion was extracted from Chapter 15 of the 8th Edition of *Air Sampling Instruments for Evaluation of Atmospheric Contaminants*, Swift and Lippman (1995).

Introduction

Separation of particles from an air stream using electrostatic precipitators is based on the use of electrostatic forces. Since the electrostatic force is placed directly on the particles instead of on the entire gas volume, relatively less energy is needed to collect the particles or to move the gas stream through the collector, compared to other collection mechanisms. For example, in the case of inertial collectors, most of the energy is used to drive the gas through the collector, and high collection efficiency is reflected in very high pressure drops.

Two advantages of electrostatic precipitator samplers compared to filter samplers are: (1) the sampling rate is not affected by mass loading, and (2) the collected sample is in a readily recoverable form. In one type of precipitator sample, the particles are collected on a large surface, where the surface may be covered by a paper or a liquid film depending on the follow-up analysis. On a second type of electrostatic sampler, the electron microscope grid sampler, the sampler collects small samples for particle size distribution analyses. This type of sampler collects representative samples quickly without sample losses and alterations that occur when transferring membrane filter samples to electron microscope grids.

Principles of Electrostatic Precipitation

Two operations are involved in collecting particles by electrostatic precipitation: electrically charging the particles and accelerating the charged particles toward an oppositely charged electrode. A number of mechanisms for charging particles have been used, including friction with solid material, flame ionization, radioactive charging, and high-voltage corona discharge. The most widely used mechanism is the corona discharge because of its efficiency, speed, and controllability. Figure 4-27 shows an axial view of high-voltage corona discharge. The electric field close to the high voltage wire speeds up free electrons that ionize the gas molecules which end up with the corona glow. The affinity of the charged particles toward the collecting electrode depends on the number of charges acquired, the viscous drag of the air, and the electric field strength.

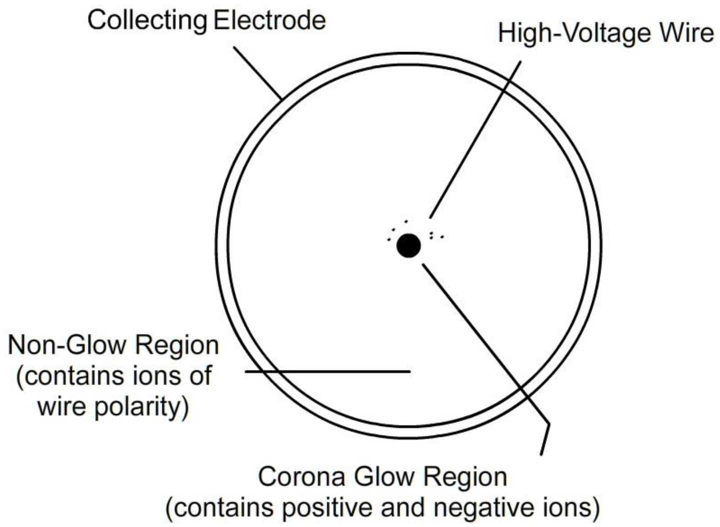

Figure 4-27. Axial view of high voltage corona discharge.

Collection Efficiency

Variables affecting the collection efficiency of electrostatic samplers include such items as current, flow rate, voltage, particle size, particle shape, particle concentration, humidity, pressure, and temperature. High-charging currents, high-voltage gradients, and low flow rates improve the collection efficiency, while very high humidity reduces the collection efficiency because of electrical breakdown that occurs in a humid atmosphere. Maintaining as high a voltage as possible during the entire sampling period, without inducing excessive sparking, will result in the maximum collection efficiency.

Specific Applications

Electrostatic precipitator samplers have been developed for a number of applications, including mass concentration analysis, sampling for radioactive particles, and sampling for particle size analysis. In the past, a field instrument employing a negative corona central electrode was used for the collection of atmospheric samples that allowed for gravimetric mass analysis and subsequent particle speciation. Also, high-volume samplers with sampling rates as high as 10,000 L/min have been designed for gravimetric and other particle analysis. Using this sampler, particles were collected on a rotating plate coated with a thin film of liquid. Swift and Lippman (1995) report that instruments employing electrostatic sampling have been used for the sampling of radioactive particles. Also, because particles travel at various distances in an electrostatic sampler before reaching a grounded collector, variations in particle size occur along the length of a simple coaxial precipitator. This aspect allows for particle size analysis using the electrostatic precipitator. However, the particle travel distance is also influenced by other variables, such as the linear air velocity in the tube, radial position at which the particle enters the tube, particle dielectric properties, ion density, and voltage gradient. A discussion of several particle sizing electrostatic precipitator samplers is also included in the Swift and Lippman (1995) reference.

4.8 Thermal Precipitators

Introduction

Thermal precipitators collect particles from an air stream by passing the air sample through a narrow channel having a significant temperature gradient perpendicular to the direction of flow. The particles move towards the decreased temperature surface and deposit on it, allowing for subsequent analysis of the collected particles. Figure 4-28 illustrates a schematic view of a thermal precipitator.

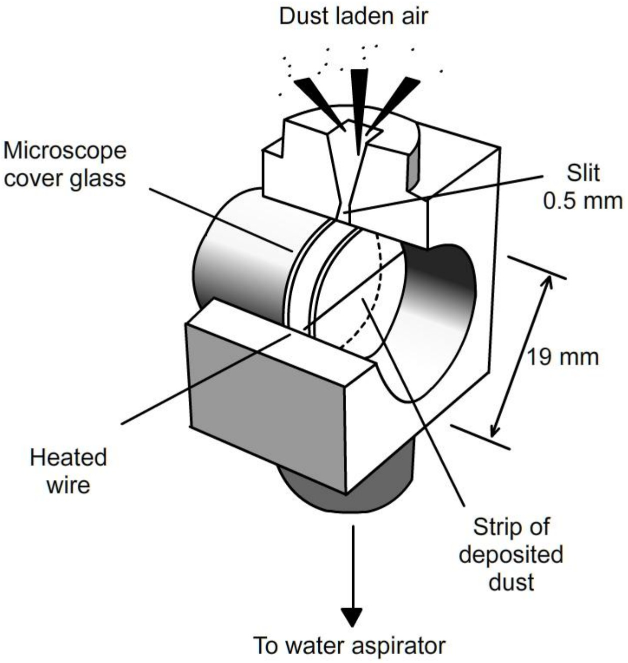

Figure 4-28. Sampling head of thermal precipitator.

Collection Efficiency and Deposition Pattern

Generally all particles 5 to 0.005 μm and less in diameter are collected in a thermal precipitator sampler, provided that the thermal gradient is about 104 K/cm. For particles larger than 5 μm, gravitational and inertial effects may interfere with the collection efficiency. Also, at wind speeds greater than 6 m/sec, the sample collection efficiency will be reduced. It is interesting to note that because the deposition pattern of particles on the collection surface in a direction parallel to air flow is Gaussian, the particle concentration can be determined by extrapolation of the spatial distribution curve.

Advantages and Disadvantages of Thermal Precipitators

The major advantage of the thermal precipitator is the extremely high collection efficiency, particularly in comparison to liquid impingers and cascade impactors. Also, the low sampling velocity prevents the shattering or breakup of the collected particles during the sampling cycle and particles may be collected on a wide variety of surfaces, allowing for numerous types of special analysis including optical microscopy, electron microscopy, photometry, and radioactivity. Disadvantages of the sampler are that the low sampling rate renders the sampler unsuitable for some analysis, volatile aerosols cannot be collected, and the standard thermal precipitator has poor size selection characteristics. This latter disadvantage is especially important if too large a sample size is taken.

4.9 Summary

This chapter focused on the fundamental principles commonly associated with sampling for PM in the atmosphere. These sampling principles—impaction, centrifugal separation, filtration, diffusion, interception, gravitational settling, and electrical and thermal precipitation—provide for the separation of the particle size fraction of interest from the sample gas stream and are the basis for the operational design of PM sampling instrumentation. In most cases, one or more of the principles are utilized within a sampling instrument in order to properly characterize the particle size fractions of concern.

In Chapter 5, the discussion of PM sampling continues as it relates to specific PM sampling and monitoring instruments, primarily focusing on instruments commonly found at federal, state, local, and tribal PM monitoring locations. These instruments include FRM and FEM samplers for TSP, PM_{10}, and $PM_{2.5}$; $PM_{2.5}$ speciation samplers; and continuous, automated instruments.

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Chapter

5

Methodologies and Instrumentation for Particulate Matter Sampling

This chapter will take approximately 3.5 hours to complete.

OBJECTIVES

Terminal Learning Objective

At the end of the chapter, the student will be able to describe the methods and instruments used in particulate matter sampling.

Enabling Learning Objectives

5.1 Understand overview of chapter.
5.2 Describe high-volume sampling for suspended particulate matter (SPM) and air toxics.
5.3 Describe high-volume air sampling.
5.4 Describe the FRM for the determination of particulate matter as PM_{10}.
5.5 Identify the FRM and FEM for the determination of fine particulate matter as $PM_{2.5}$.
5.6 Identify the FRM and FEM for the determination of coarse particles (PM_{10}-$PM_{2.5}$).
5.7 Describe the procedures for $PM_{2.5}$ speciation sampling.
5.8 Explain the procedures for *in situ* monitoring for particulate matter.
5.9 Describe automated Federal Equivalent Monitors.
5.10 Describe additional automated PM methods.

5.1 Introduction

In this chapter, the sampling principles discussed in Chapter 4 are applied to a discussion of the design and operation of PM samplers commonly used at monitoring sites, as well as PM samplers developed to accommodate other sampling needs. Specifically, Federal Reference Method (FRM) methods are discussed for TSP (today used primarily to monitor ambient lead and air toxics), PM_{10}, $PM_{2.5}$, and PM_{10}-$PM_{2.5}$. In addition to the FRM methods, continuous monitoring instruments, several of which are approved as FEMs for PM_{10} and $PM_{2.5}$, are discussed in this chapter. The continuous instruments are increasingly being utilized at monitoring locations due to their ability to provide time-resolved PM mass concentration. This chapter also discusses filter-based $PM_{2.5}$ speciation samplers, which are capable of providing elemental or compound- specific particulate mass concentration.

5.2 High-Volume Sampling for Suspended Particulate Matter (SPM) and Air Toxics

When air pollution control agencies attempt to determine the nature and magnitude of air pollution in their communities and the effectiveness of their control programs, they collect samples of suspended, inhalable, and respirable particulate matter (PM). Suspended particulate matter (SPM) in air generally is a complex, multi-phase system of all airborne solid and low-vapor pressure liquid particles having aerodynamic particle sizes from below 0.01 µm to 100 µm and larger. Inhalable PM is the fraction of suspended particulate matter (SPM) that is capable of being respired into the human respiratory system in significant quantities, described as particles with an aerodynamic diameter of less than 10 µm (i.e., PM_{10}). This size fraction is more commonly referred to as *coarse* particles or *thoracic coarse* particles. Another subset of SPM includes a size fraction of particles with an aerodynamic diameter of the less than 2.5 μm, which is referred to as respirable PM. The smaller particles ($PM_{2.5}$) are able to reach the lower regions of the human respiratory tract and, thus, are responsible for most of the adverse health effects associated with suspended particulate pollution. This size fraction is more commonly referred to as *fine* particles.

Alternatively, atmospheric particles can be identified based on the two distinct modes in which they occur: the fine (<2.5 μm) mode and the coarse (2.5-10.0 μm) mode. The fine or accumulation mode (or respirable particulate matter) is attributed to the growth of particles from the gas phase and subsequent agglomerization, whereas the coarse mode is made of mechanically abraded or ground particles. Because of their initially gaseous origin, the fine range of particle sizes includes inorganic ions such as sulfate, nitrate, and ammonia, as well as combustion-form carbon, organic aerosols, metals, and other combustion products. Coarse particles, on the other hand, normally consist of finely divided minerals such as oxides of aluminum silicate, iron, calcium, and potassium.

EPA's approach toward regulating and monitoring SPM in ambient air has evolved over time. Initially, the EPA was concerned about total concentrations of SPM (i.e., TSP, or total suspended particulate matter) and lead (Pb); more recently, however, interest has focused on smaller particles ($PM_{2.5}$) as well as other types and quantities of various organic and inorganic components of SPM.

Several different sampling techniques and devices—filtration, electrostatic and thermal precipitation, and inertial separators (by means of actual and "virtual" impaction)—may be employed to collect suspended particulate pollutants from ambient air. Of the various techniques, filtration and inertial separation have been found to be the most suitable for routine air sampling. The so-called high-volume (hi-vol) sampler remains in use for the determination of TSP, PM_{10}, and organic/inorganic components of SPM as determined by post-sampling chemical analysis. The EPA has designated the high-volume method as the reference method for total suspended particulate matter (TSP) and PM_{10} when outfitted with a size selective inlet. The reference method for the determination of lead in SPM prescribes a 24-hour sampling period and procedures identical to that of the high-volume reference methods.

The reference methods for TSP, PM_{10}, $PM_{2.5}$, and lead are codified in 40 CFR 50, Appendix B, J, L, and G, respectively. In these methods, a known volume of air is drawn through the sampler and the particulate fraction of interest (TSP, PM_{10}, or $PM_{2.5}$) is collected. The mass of particulate matter subsequently is determined gravimetrically and the average ambient concentration over the sampling period is calculated. The collected material can be analyzed to determine the identity and quantity of inorganic (metal) and organic compounds present in the TSP (i.e., SPM) sample. The choice of analytical method will depend on the compounds of interest and the detection limits desired. Some analytical techniques are used only with particular sampling methods. Furthermore, the type of filter medium used to capture the sample is a factor in the choice of analytical technique, and vice-versa.

A detailed discussion of appropriate sampling methodology and analytical technique regarding the determination of organic and inorganic compounds associated with SPM can be found in the Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air, EPA/625/R-96/01a, July 1999 (http://www.epa.gov/ttn/amtic/inorg. html) and the Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, EPA/625/R-96/010b, January 1999 (http://www.epa.gov/ttn/amtic/files/ ambient/airtox/tocomp99.pdf). Table 5-1 summarizes specific sampling and analytical methods which utilize the high-volume method to sample particulate matter, metals, and semi-volatile compounds.

Table 5-1. Summary of sampling and analytical methods utilizing the high-volume method to sample PM, metals, and semi-volatile compounds.

Method	Pollutant or Pollutant Category	Sample Collection Media
TSP [1]	TSP	quartz filter
PM10 [2]	PM_{10}	quartz filter
Lead (Pb) [3]	Lead (Pb)	quartz filter
TO-4A [4]	Pesticides & PCBs	PUF cartridge
TO-9A [4]	Dioxins & furans	quartz filter & PUF cartridge
TO-13A [4]	PAHs	quartz filter & PUF cartridges or XAD-2™
IO-3.1 [5]	metals	quartz filter, other
IO-3.2 [5]	metals	quartz filter
IO-3.4 [5]	metals	quartz filter
IO-3.5 [5]	metals	quartz filter
IO-3.6 [5]	metals	quartz filter
IO-3.7 [5]	metals	quartz filter

Note 1: Reference Method for the Determination of Suspended Particulate Matter in the Atmosphere (High-Volume Method). Found in 40 CFR 50, Appendix B.

Note 2: Reference Method for the Determination of Particulate Matter as PM_{10} in the Atmosphere. Found in 40 CFR 50, Appendix J.

Note 3: Reference Method for the Determination of Lead in Suspended Particulate Matter Collected from Ambient Air (High-Volume Method). Found in 40 CFR 50, Appendix G.

Note 4: Methods described in the Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air (Second Edition), EPA/625/R-96/010b, January 1999.

Note 5: Methods described in the Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air, EPA/625/R-96/01a, July 1999.

5.3 High-Volume Air Sampling

Introduction

The so-called high-volume (hi-vol) sampler for total suspended particulate matter (TSP) was previously the most widely used sampler since it was the Federal

Reference Method (FRM) for measuring compliance with the TSP particulate matter standard. Approximately 20,000 hi-vols were operating at federal, state, and local air pollution control agencies, industries, and research organizations for either routine or intermittent use in the 1970's. As TSP levels decreased, the number of TSP samplers in operation greatly diminished. With the promulgation of the PM_{10} standard in 1987, the number of TSP samplers operated by state and local agencies was down to approximately 2800 and the number of PM_{10} samplers was 636. By 1997 the number of TSP samplers operated by state and local control agencies was reduced to approximately 450. Although there is no TSP standard, the TSP FRM remains as the official sampling method for obtaining samples to determine compliance with the national ambient air quality standard for lead.

Development of the High-Volume Sampler

In 1948, Silverman (Silverman and Viles 1948) developed an aerosol collector that consisted of a household vacuum sweeper motor encased in an airtight sheet metal housing adapted to hold a 4-inch diameter filter. Provision was made for measuring the air flow through the system. Because this sampler operated at a much higher flow rate than other available samplers, it was identified as a high-volume sampler, and the designation persists. Replacement of the thin sheet metal motor housing with one of cast aluminum by the Staplex Company in the early 1950s improved the Silverman sampler. Adoption of a stainless steel filter holder to accommodate an 8- by 10-inch filter permitted 24-hour operation of the sampler and collection of a much larger sample of particulate matter than was previously possible (Figure 5-1).

Although the Staplex sampler performed satisfactorily, it was decided after several years of experience that a more rugged sampler was needed to meet the requirements of a large-scale sampling network operation. Accordingly, in 1957, a new high-volume sampler, developed in collaboration with General Metal Works, was introduced. The new sampler used a different motor that was completely enclosed in a cast aluminum housing, eliminating the sheet metal and rubber components used in the Staplex sampler, thus simplifying brush and motor replacement. This sampler and others similar to it were widely accepted.

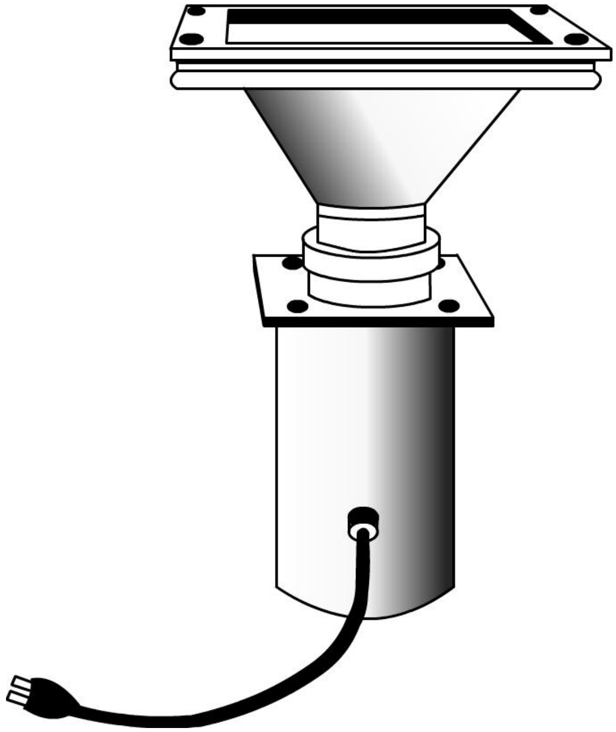


Figure 5-1. Hi-vol sampler components (motor, filter, housing).

Sampler-Shelter Combination

The sampler and its shelter should be considered as a single, functioning unit (Figure 5-2). The shelter must provide protection for the sampler, and at the same time allow unrestricted access of ambient air from all directions without direct impingement of particles on the filter. A high-volume sampler with a 7- by 9-inch exposed filter area operated in a standard shelter at a sampling flow rate of 1.1 to 1.7 cubic meters per minute (39 to 60 cubic feet per minute) collects particles of up to 25 to 50 μm in aerodynamic diameter, depending on wind speed and direction, and uniformly distributes the sample over the filter surface. The standard peak roof of the shelter, which acts as a plenum above the filter, is placed to provide a total opening area of slightly more than the 63-square-inch exposed filter area, thereby permitting free flow of air into the plenum space (Figure 5-3).

The size of the opening to the filter and the volume of air filtered per unit time will affect the particle size range collected. Distribution of particles on the filter may also be affected. Therefore, any high-volume sampler purchased after February 3, 1983, and used for federally mandated air monitoring, must have uniform sample air inlets that are sized to provide an effective particle capture air velocity of between 20 and 35 cm/sec at their recommended sampling flow rates. The particle capture air velocity is determined by dividing the sample air flow rate by the inlet area measured in a horizontal plane at the lower edge of the sampler's roof. Ideally, the inlet area and sampling flow rate of these samplers should be selected to obtain a capture air velocity of 25 ± 2 cm/sec.

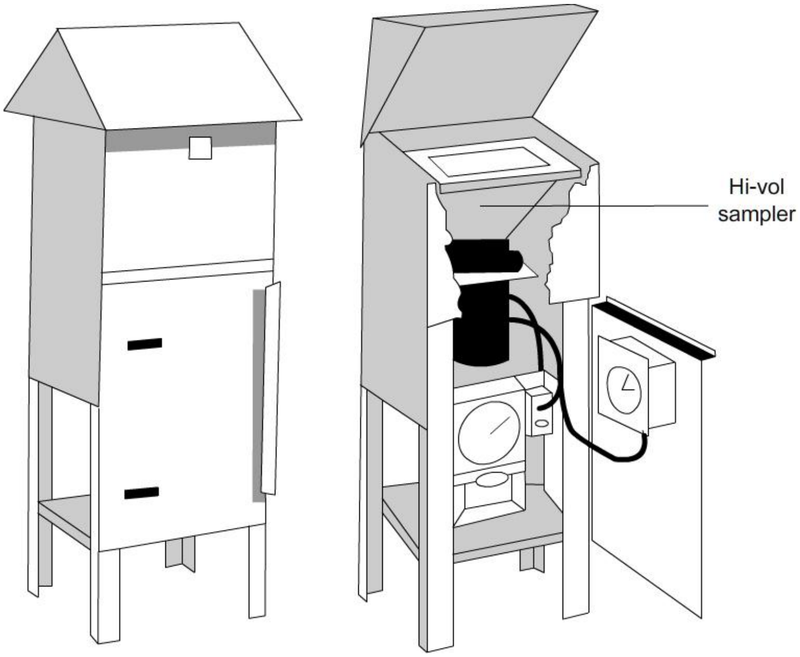


Figure 5-2. Hi-vol sampler in shelter.

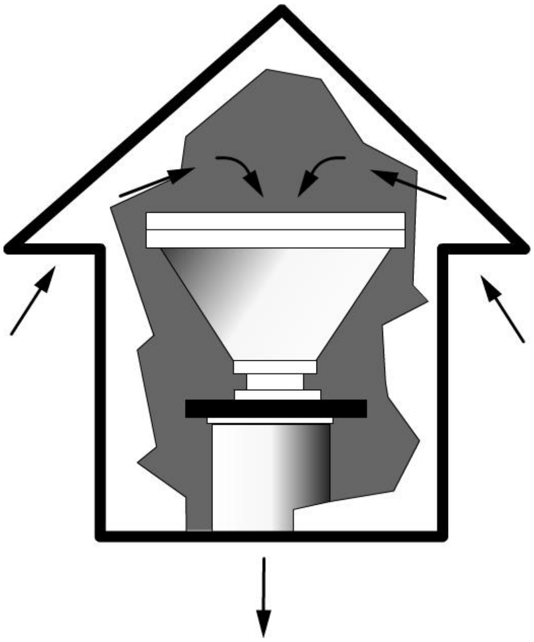


Figure 5-3. Air flow of hi-vol sampler in shelter.

Filter Media for High-Volume Sampler

Choice of filter media is influenced by the objectives of the sampling program and the characteristics of the sampler to be employed. An excellent discussion of filter media and filtration sampling is presented in *Air Sampling Instruments* (American Conference of Governmental Industrial Hygienists, 2001), "EPA

Guideline on Speciated Particulate Monitoring" (1998, Draft), and Chapter 4 of this Student Manual.

Glass fiber filters have been extensively used for total suspended particulate matter sampling. Such filters have a collection efficiency of at least 99% for particles having aerodynamic diameters of 0.3 μm and larger, low resistance to air flow, and low affinity for moisture, all of which are distinct advantages during sampling. However, in order to eliminate possible weight errors due to small amounts of moisture, both unexposed and exposed filters should be equilibrated between 15°C and 30°C with less than ± 3°C variation, at a relative humidity below 50% with less than ± 5% variation, for 24 hours before weighing.

Samples collected on glass fiber filters are suitable for the analysis of a variety of organic pollutants and a large number of inorganic contaminants, including trace metals and several nonmetallic substances. Also, glass fiber filters are excellent for monitoring gross radioactivity. However, satisfactory analyses for materials already present in substantial amounts in the filter are not possible. A random, but statistically significant, sample of new filters should be analyzed to determine whether the filter blank concentration is high enough to interfere with a particular analysis. It is wise to obtain this information before purchasing large numbers of filters to avoid potential problems caused by high filter blanks.

While glass fiber filter material has been dominant in the measurement of total suspended particulate matter, numerous applications have been found for cellulose filters. Cellulose filters have relatively low metal content, making them a good choice for metals analysis by neutron activation, atomic absorption, emission spectroscopy, etc. Conventional high-volume samplers usually have to be modified to use cellulose filters because the filters clog rapidly, causing flow to sometimes decrease by as much as a factor of two during a one-day sampling interval. Other disadvantages of cellulose are its absorption of water and enhanced artifact formation of nitrates and sulfates. These disadvantages can usually be overcome by using a control blank filter. Spectro-quality grade glass fiber filters have sufficiently low background metal content to make them acceptable for metal analysis, if cellulose cannot be used.

Filters used for federally-mandated TSP sampling must meet the specifications listed in Table 5-2. Filters supplied by the U.S. EPA can be assumed to meet these specifications.

Table 5-2. U.S. EPA specifications for TSP filters. Additional specification for TSP filters used for the determination of lead in SPM.

Size	$20.3 \pm 0.2 \times 25.4 \pm 0.2$cm (nominal 8×10 in.)
Nominal exposed area	406.5 cm^2 (63 in.^{2})
Material	Glass fiber filter or other relatively inert, nonhygroscopic material
Collection efficiency	99% minimum is measured by the DOP test (ASTM-2986) for particles of 0.3-μm aerodynamic diameter

Recommended pressure drop range	42 to 54 mm Hg (5.6 to 7.2 kPa) at a flow rate of 1.5 std m^3/min through the nominal exposed area
pH	6 to 10
Integrity	2.4 mg maximum weight loss
Tear strength	500 g minimum for 20-mm wide strip cut from filter in weakest dimension (ASTM Test D828-60)
Brittleness	No cracks or material separations after single lengthwise crease
Lead content	Low Pb concentration desirable (typical Pb content 75 μg/filter). Low degree of Pb content variability between filters of the same batch.

Precautions in Filter Handling

After the desired filters have been chosen, each should be permanently identified by stamping a serial number on two diagonally opposite corners (one number on each side of the filter). Care should be taken not to tear the filter when affixing the identification number. Filters should then be inspected visually for holes, tears, particles, or other imperfections that may cause uneven loading, loss of particulate matter, or other failure during the sampling period. A backlighting device, such as a light table, should be used during the inspection.

Before the filters are weighed, they should be equilibrated for at least 24 hours in a conditioning environment (15°C to 30°C not to vary more than ± 3°C, relative humidity less than 50% not to vary more than ± 5%) free of acidic or basic gases that might react with the filter material. The analytical balance used for the weighing should be calibrated with three to five standard weights over a range including the expected weights of unexposed and exposed filters. The filters should be taken directly from the conditioning chamber to the balance to minimize the risk of contaminating the filter. They should then be weighed to the nearest milligram, and the weight and number of each filter should be recorded. Filters must not be folded or creased before use, as this may establish erroneous flow patterns during sampling.

To install a clean filter in the sampler, the wing nuts are loosened and the faceplate is removed (Figure 5-4). The filter, with its rough side up, should be centered so that the gasket forms an airtight seal on the outer edge of the filter when the faceplate is in position. The faceplate is then replaced and the wing nuts are tightened. The gasket should not be tightened to the point that filter damage might occur. Hi-vol filter cartridges similar to the one pictured in Figure 5-5 make installation of filters easier. Installation and removal of a filter can be performed inside a building, thus eliminating handling problems due to lack of space and windy conditions.

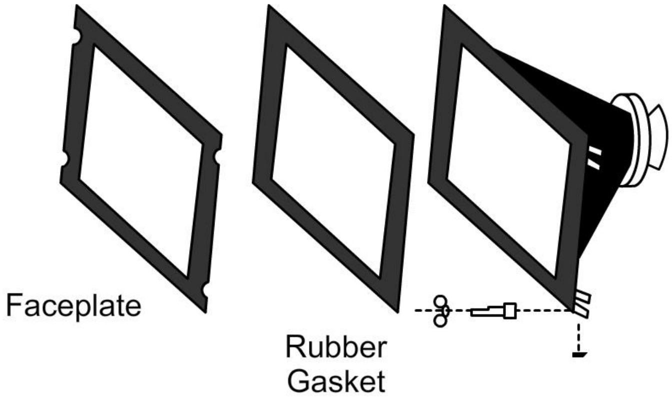


Figure 5-4. Hi-vol sampler filter adapter assembly.

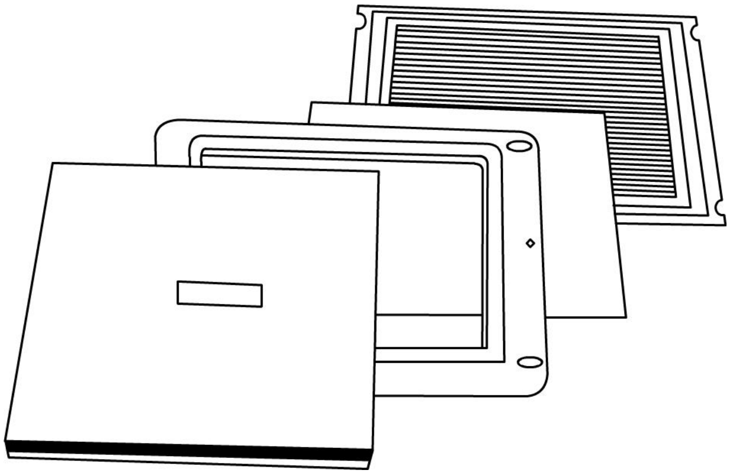


Figure 5-5. Hi-vol filter cartridge.

When the filter is removed, it should be checked for holes or other physical damage and foreign material (such as insects). Caution should be observed to minimize filter damage when removing the faceplate and the gasket. If the filter's border appears fuzzy or nonexistent, there may be an air leak around the gasket. The sample should be voided and the gasket checked. After the visual check, the filter should be folded in half lengthwise so that sample touches sample. This minimizes sample loss during transport to the lab. The filter is then placed in a glassine envelope or a manila folder and taken to the lab for weighing and analysis. The filter should be placed in the conditioning environment for at least 24 hours before weighing to ensure that the same humidity and temperature conditions are present during the final weighing as were present during the initial weighing.

Documentation of all these steps is for legal purposes and to ensure data reliability. The operator who starts the sampler is responsible for recording the following information:

- Filter serial number
- Sampling site identification number and/or address
- Sampler identification number
- Starting time
- Initial sampling flow rate
- Sampling date (including day, month, and year)
- Summary of conditions that may affect results (e.g., meteorology, construction activities, etc.)
- Operator's initials or signature
- Ambient temperature and barometric pressure, if necessary (see calibration section of this chapter).

The operator who removes the sample is responsible for recording the following information:

- Stop time and elapsed time (if available)
- Final sampling flow rate
- Operator's initials or signature
- Ambient temperature and barometric pressure, if necessary (see calibration section of this chapter)
- Comments concerning voided samples
- Summary of existing conditions that may affect results.

Calibration

Most high-volume samplers use an orifice/pressure indicator, an electronic mass flowmeter, or a rotameter (visifloat) for measuring sampling flow rate (Figure 5-6). All flow rate measuring devices must be calibrated against known flow rates. This is accomplished by calibrating the devices with a flow rate transfer standard that has been calibrated with a positive-displacement standard volume meter having a calibration that is traceable to the National Institute of Standards and Technology.

The U.S. EPA has specified procedures in Appendix B of 40 CFR 50 for the calibration of orifice-type flow rate transfer standards as well as the calibration of sampler flow rate measuring devices. These procedures are described below.

A flow rate transfer standard is calibrated by attaching it by means of a filter adapter to the inlet of a positive-displacement standard volume meter, such as a Roots meter (Figure 5-7). Air is then drawn through the transfer standard and the standard volume meter by a high-volume air pump, such as a high-volume sampler motor, attached to the outlet of the standard volume meter. Air should be drawn at a minimum of five different, but constant, evenly distributed flow rates, with at least three of the flow rates within a range of 1.1 to 1.7 m^3/min (39 to 60 ft^3/min). The flow rates are determined by timing the flow of a known volume (at least 3 m^3) of air through the transfer standard as indicated by the standard volume meter.

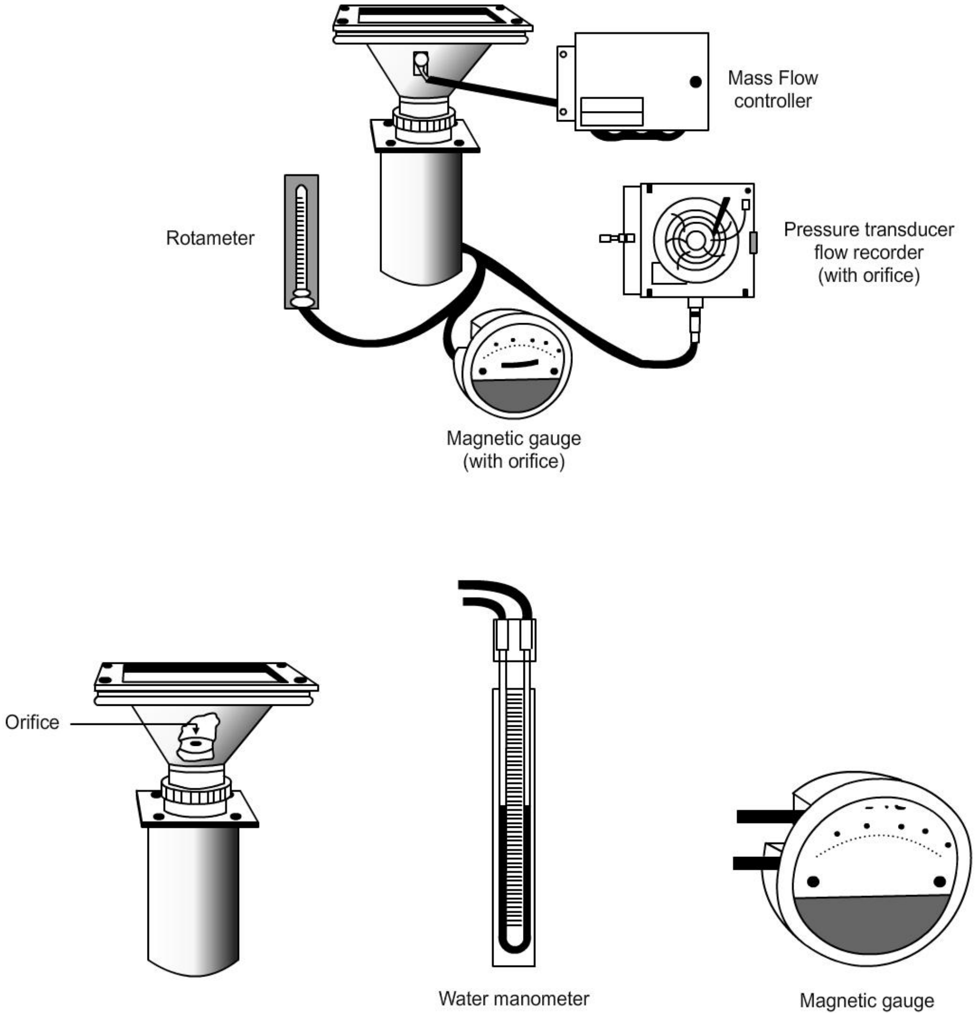


Figure 5-6. Typical flow rate indicating devices.

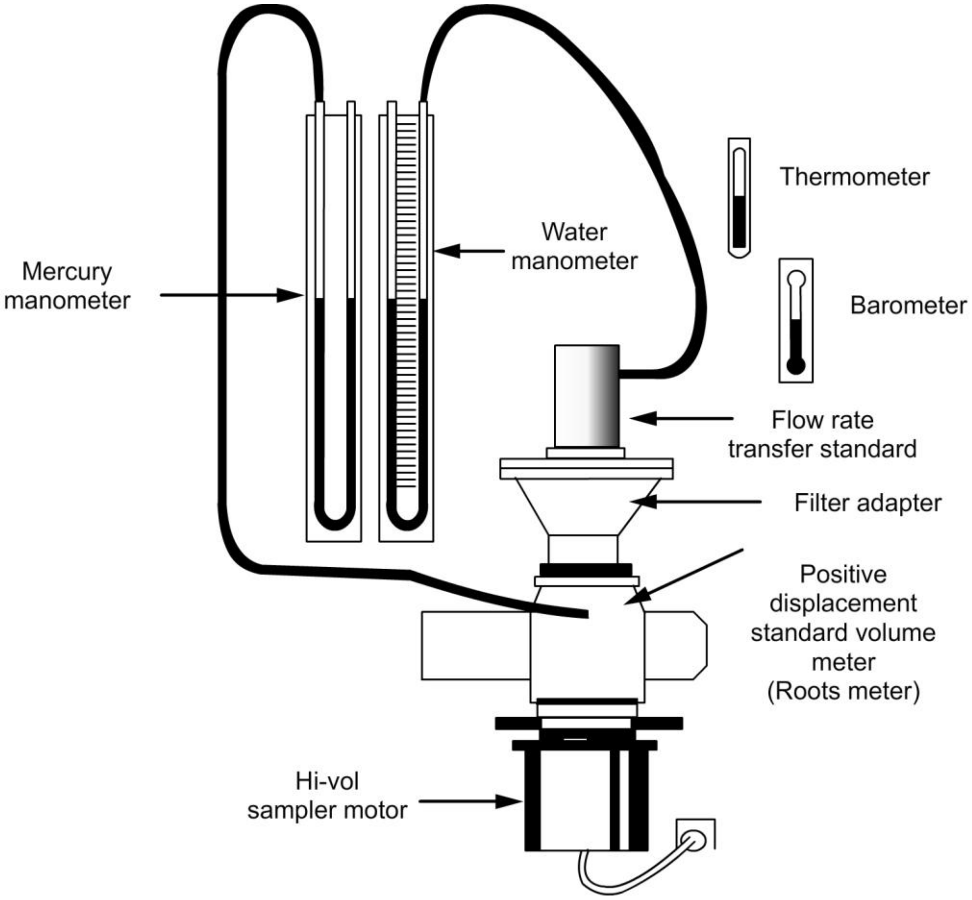


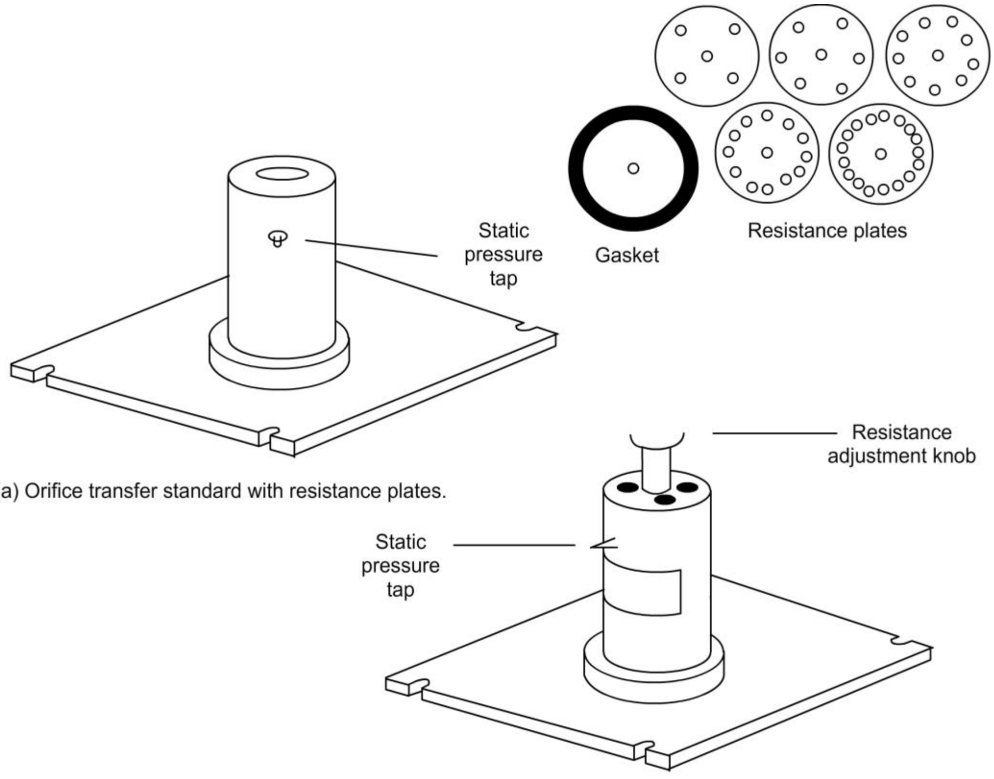
Figure 5-7. Flow rate transfer standard calibration setup.

Air passing through the orifice-type transfer standard causes a pressure drop that varies directly with flow rate (i.e., pressure drop increases as flow rate increases). The pressure drop (ΔH) associated with each flow rate of air through the transfer standard is measured by means of a water manometer that is attached to the static pressure tap of the transfer standard.

A pressure drop is also caused in the standard volume meter by air passing through it. However, this pressure drop varies inversely with flow rate (i.e., pressure drop decreases as flow rate increases). The pressure drop (ΔP) associated with each flow rate of air through the standard volume meter is measured by means of a mercury manometer that is attached to a static pressure tap located just below the inlet of the standard volume meter.

Before any flow rates are measured, the calibration setup is checked for air leaks by temporarily clamping both manometer lines, blocking the inlet of the transfer standard by using a rubber stopper, cellophane tape, or other suitable means, and activating the high-volume air pump. Any change in the reading of the standard volume meter indicates an air leak, which must be eliminated before proceeding with the calibration.

After all leaks have been eliminated, the high-volume air pump is deactivated, the manometers are unclamped and "zeroed," and the inlet of the transfer standard is unblocked. Different but constant flow rates are then generated by operating the high-volume air pump at a constant voltage and installing resistance plates (metal plates having differing numbers of holes) in the transfer standard (Figure 5-8a), adjusting a variable resistance plate of the transfer standard (Figure 5-8b), or by varying the voltage to the high-volume air pump. If resistance plates are used, the leak check described above must be repeated each time a resistance plate is installed.



(a) Orifice transfer standard with resistance plates.

(b) Variable resistance orifice transfer standard.

Figure 5-8. Typical orifice-type flow rate transfer standards.

The air volume measured by the standard volume meter is corrected to standard volumes (std m^3) by using the following equation:

(Eq. 5-1)

$$V_{std} = V_m \frac{P_1 - \Delta P}{P_{std}} \frac{T_{std}}{T_1}$$

Where:

V_{std} = *standard volume, std* m^3

V_m = *actual volume measured by the standard volume meter*

P_1 = *barometric pressure during calibration, mm Hg or kPa*

ΔP = *pressure drop at inlet to volume meter, mm Hg or kPa*

P_{std} = *760 mm Hg or 101 kPa*
T_{std} = *298 K*
T_1 = *ambient temperature during calibration, K*

Standard flow rates are then calculated to the nearest 0.01 std m^3/min by using Equation 5-2.

(Eq. 5-2)
$$Q_{std} = \frac{V_{std}}{t}$$

Where: Q_{std} = *standard volumetric flow rate, std m^3/min*
t = *elapsed time, minutes*

After the standard flow rates have been determined, $\sqrt{\Delta H(P_1/P_{std})(298/T_1)}$ is calculated for each flow rate and plotted against its associated standard flow rate (Q_{std}). The transfer standard calibration curve is then determined either by drawing a line of best fit between the individual plotted points (Figure 5-9), or calculating the slope and y-intercept of the curve by linear least squares regression analysis.

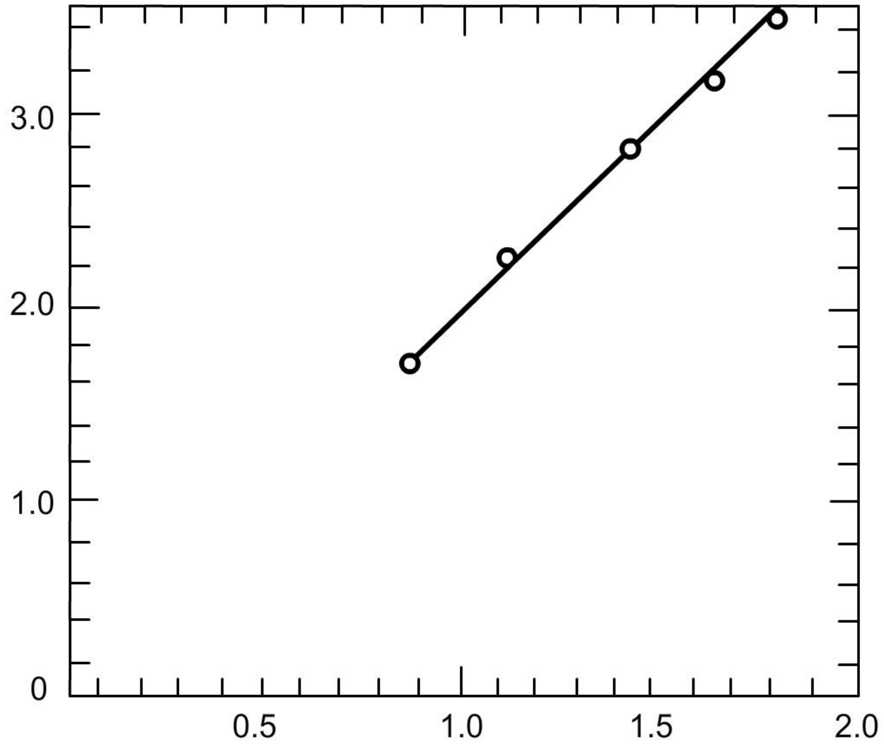


Figure 5-9. Typical calibration curve for a flow rate transfer standard.

A sampler flow rate measuring device is calibrated by attaching a calibrated flow rate transfer standard to the inlet of the device's associated high-volume sampler (Figure 5-10). It must be ensured that there are no air leaks between the transfer standard and the high-volume sampler, and the sampler must be allowed to reach thermal equilibrium. Then, air is drawn through the transfer standard and the high-volume sampler at several different, but constant, flow rates, distributed over a flow rate range that includes 1.1 to 1.7 std m^3/min by the motor of the high-volume sampler. The flow rates should not be generated by varying the voltage to the sampler's motor if an orifice-type flow rate measuring device located downstream of the motor is being calibrated.

Pressure drop (ΔH) within the transfer standard measured by a water manometer that is attached to the static pressure tap of the transfer standard, and the flow rate indication (I) of the sampler's flow rate measuring device, are recorded for each flow rate of air. Where P_2 is the barometric pressure (mm Hg or kPa) and T_2 is the ambient temperature (K) during the calibration, $\sqrt{\Delta H(P_1/P_{std})(298/T_1)}$ is calculated for each flow rate. The calculated values are then used to determine the flow rates at standard conditions (Q_{std}), either by referring to a graph of the transfer standard's calibration curve, such as Figure 5-9, or by calculating Q_{std} using the slope and y-intercept of the transfer standard's calibration curve.

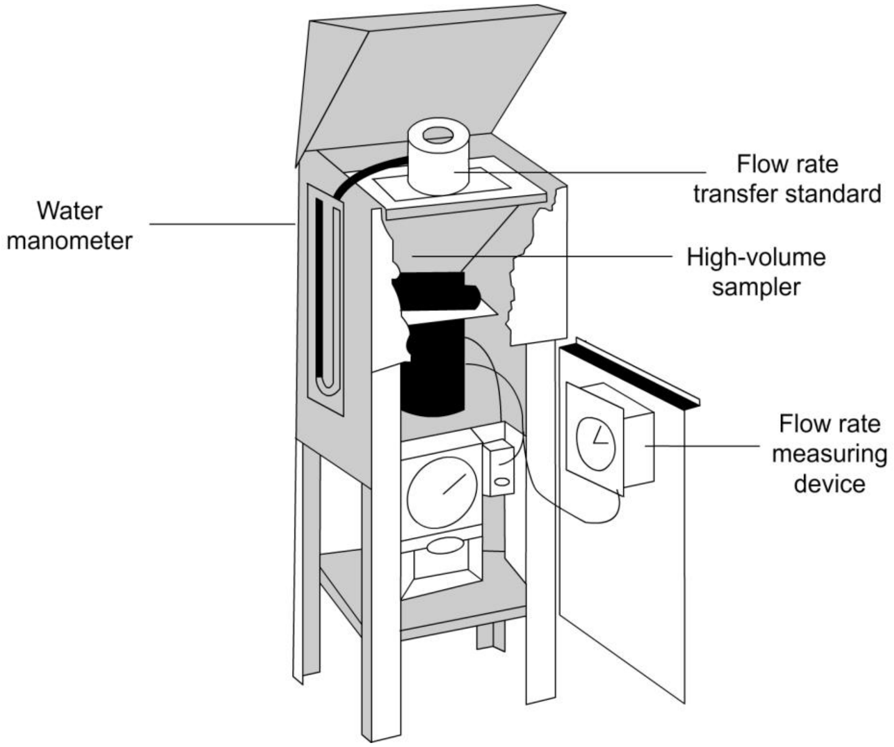


Figure 5-10. Flow rate measuring device calibration setup.

Flow rates indicated (*I*) by a sampler's flow rate measuring device are then expressed, with regard to the type of flow rate measuring device used and the method of correcting sample air volumes for ambient temperature and barometric pressure, by using the formulas of Table 5-3. The formulas for geographic average barometric pressure (P_a) and seasonal average temperature (T_a) may be used to approximate actual pressure and temperature conditions during sampling for a seasonal period, if the actual barometric pressure and temperature at the sampling site do not vary by more than ± 60 mm Hg from P_a or ± 15°C from T_a, respectively. Furthermore, P_a may be estimated from an altitude-pressure table or by making an approximate elevation correction of -26 mm Hg (-3.46 kPa) for each 305 m (1000 ft) that the sampler is above sea level (760 mm Hg or 101 kPa), and T_a may be estimated from weather station or other records.

Table 5-3. Formulas for expressing indicated flow rates of sampler flow rate measuring device calibration.

	Expression	
Type of sampler flow rate measuring device	**For actual pressure (P_2) and temperature (T_2) corrections**	**For incorporation of geographic average barometric pressure (P_a) and seasonal average temperature (T_a)**
Mass flowmeter	I	I
Orifice and pressure indicator	$\sqrt{I\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$	$\sqrt{I\left(\frac{P_2}{P_a}\right)\left(\frac{T_a}{T_2}\right)}$
Rotameter, or orifice and pressure recorder having a square root scale*	$\sqrt{I\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$	$\sqrt{I\left(\frac{P_2}{P_a}\right)\left(\frac{T_a}{T_2}\right)}$

* This scale is recognizable by its non-uniform divisions and is the most commonly available for high-volume samplers.

After the flow rates indicated by the sampler's flow rate measuring device have been properly expressed, the resulting values are plotted against their associated standard flow rates (Q_{std}). The calibration curve for the sampler flow rate measuring device is then determined either by drawing a line of best fit that is readable to 0.02 std m^3/min between the individual plotted points (Figure 5-11) or by calculating the slope, y-intercept, and correlation coefficient of the curve by linear least squares regression analysis.

The calibration of flow rate measuring devices of high-volume samplers having flow controllers depends on the operating histories of the samplers. Flow-controlled samplers having operating histories demonstrating that their flow rates are stable and reliable may be calibrated solely at their controlled flow rates by using a clean (unexposed) filter (i.e., calibrated at only one flow rate near the lower limit of the controlled flow rate range). In these cases, the sampler flow rate measuring devices may remain uncalibrated at flow rates outside their controlled flow rate ranges, but they should be used to indicate any relative change between initial and final sampling flow rates, and frequently recalibrated at their controlled flow rates to minimize potential loss of samples because of controller malfunctions. Flow rate measuring devices of flow-controlled samplers not having operating histories as described above are calibrated at several flow rates, as described previously for non-flow-controlled samplers, except that their flow controllers are disabled before calibration.

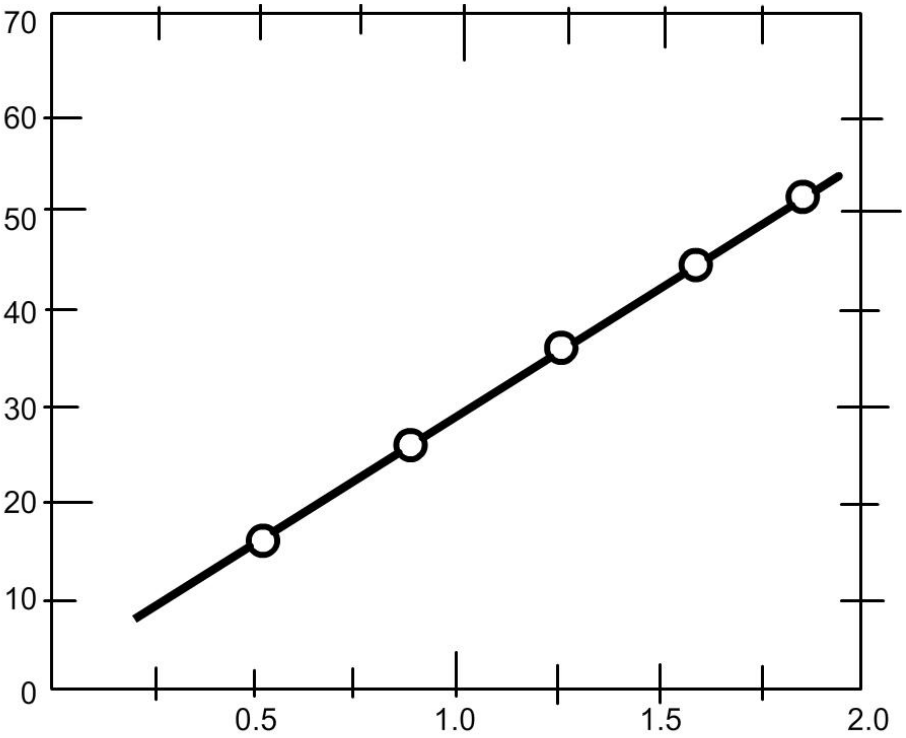


Figure 5-11. Typical calibration curve for a sampler flow rate measuring device.

Whichever calibration procedure is used for flow-controlled samplers, the abilities of their flow controllers should be verified after their calibrations. If a sampler is calibrated at several flow rates, its flow controller should be re-enabled after the calibration and a clean filter should be installed to verify its controlled sampling flow rate. After the sampling flow rate has been verified, two or more filters should be stacked and added to the sampler to determine if the flow controller maintains the controlled sampling flow rate. For a sampler that is calibrated only at its controlled sampling flow rate, one or two additional filters should be stacked and installed after the calibration to verify that the flow controller maintains the controlled sampling flow rate.

Flow rate transfer standards (e.g., Figure 5-12) and sampler flow rate measuring devices that are not described in the calibration procedures of Appendix B of 40 CFR 50, but meet specifications described in Appendix B and have U.S. EPA-calibration procedures, may be used for federally-mandated air monitoring.

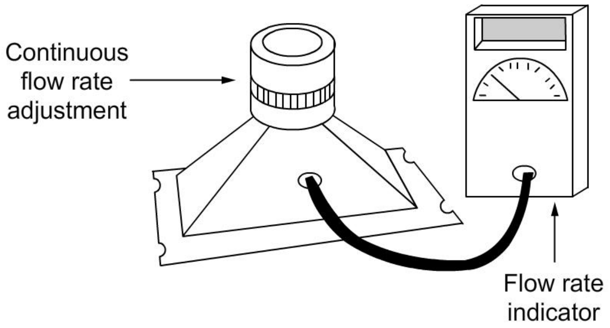


Figure 5-12. Electronic flowmeter transfer standard with externally adjustable resistance.

U.S. EPA High-Volume Sampling Procedure for TSP (Appendix B of 40 CFR 50)

The following procedure is specified in Appendix B of 40 CFR 50 for the sampling of suspended particulate matter.

1. Number each filter, if not already numbered, near its edge with a unique identification number.
2. Backlight each filter and inspect for pinholes, particles, and other imperfections; filters with visible imperfections must not be used.
3. Equilibrate each filter for at least 24 hours.
4. Following equilibration, weigh each filter to the nearest milligram and record this tare weight (W_1) with the filter identification number.
5. Do not bend or fold the filter before collection of the sample.
6. Open the shelter and install a numbered, pre-weighed filter in the sampler, following the supplier manufacturer's instructions. During inclement weather, precautions must be taken while changing filters to prevent damage to the clean filter and loss of sample from or damage to the exposed filter. Filter cartridges that can be loaded in the laboratory may be used to minimize this problem.
7. Close the shelter and run the sampler for at least five minutes to establish run-temperature conditions.
8. Record the flow indicator reading and, if needed, the barometric pressure (P_3) and the ambient temperature (T_3).
9. Stop the sampler.
10. Determine the sampler flow rate. If it is outside the acceptable range (1.1 to 1.7 m^3 min [39 to 60 ft^3/min]), use a different filter, or adjust the sampler flow rate. Warning: Substantial flow adjustments may affect the calibration of the orifice-type flow indicators and may necessitate recalibration.

11. Record the sampler identification information (filter number, site location or identification number, sample date, and starting time).
12. Set the timer to start and stop the sampler so that the sampler runs 24 hours, from midnight to midnight (local time).
13. As soon as practical following the sampling period, run the sampler for at least five minutes to again establish run-temperature conditions.
14. Record the flow indicator reading and, if needed, the barometric pressure (P_3) and the ambient temperature (T_3).

    Note: No onsite pressure or temperature measurements are necessary if the sampler flow indicator does not require pressure or temperature corrections (e.g., a mass flowmeter) or if average barometric pressure and seasonal average temperature for the site are incorporated into the sampler calibration. For individual pressure and temperature corrections, the ambient pressure and temperature can be obtained by onsite measurements or from a nearby weather station. Barometric pressure readings obtained from airports must be station pressure, not corrected to sea level, and may need to be corrected for differences in elevation between the sampler site and the airport. For a sampler having flow recorders but not constant flow controllers, the average temperature and pressure at the site *during the sampling period* should be estimated from weather bureau or other available data.
15. Stop the sampler and carefully remove the filter, following the sampler manufacturer's instructions. Touch only the outer edges of the filter.
16. Fold the filter in half lengthwise so that only surfaces with collected particulate matter are in contact and place it in the filter holder (glassine envelope or manila folder).
17. Record the ending time or elapsed time on the filter information record, either from the stop set point time, from an elapsed time indicator, or from a continuous flow record. The sample period must be 1440 ± 60 min for a valid sample.
18. Record on the filter information record any other factors, such as meteorological conditions, construction activity, fires or dust storms, etc., that might be pertinent to the measurement. If the sample is known to be defective, void it at this time.
19. Equilibrate the exposed filter for at least 24 hours.
20. Immediately after equilibration, reweigh the filter to the nearest milligram and record the gross weight with the filter identification number.
21. Determine the average sampling standard flow rate (Q_{std}) during the sampling period. If the sampler has a continuous flow rate recorder, determine the average indicated flow rate (I) for the sampling period from the recorder trace. Express I with regard to the type of flow rate measuring device used and the method of correcting sample air volumes for ambient temperature and barometric pressure by using the formulas of Table 5-3. Use the resulting value to determine Q_{std}, either by referring to a graph of the calibration curve for the sampler flow rate measuring device or by calculating Q_{std} using the following equation:

(Eq. 5-3)
$$Q_{std} = \frac{Expressed\,value\ of\ I - b}{m}$$

Where:
Q_{std} = standard volumetric flow rate, std m^3/min
I = indicated flow rate
b = y-intercept of calibration curve for sampler flow rate measurement device
m = slope of calibration curve for sampler flow rate measurement device

If the sampler does not have a continuous flow rate recorder, express the initial and final indicated flow rates (*I*) with regard to the type of flow rate measuring device used and the method for correcting sample air volumes for ambient temperature and barometric pressure using the formulas of Table 5-4. Use the resulting values to determine the initial and final sampling standard flow rates (Q_{std}) either by referring to a graph of the calibration curve for the sampler's flow rate measuring device or by calculating initial and final Q_{std} using Equation 5-3.

Table 5-4. Formulas for expressing indicated sampling flow rates.

Type of sampler flow rate measuring device	Expression	
	For actual pressure (P_3) and temperature (T_3) corrections	**For use when geographic average barometric pressure and seasonal average temperature have been incorporated into the sampler calibration**
Mass flowmeter	I	I
Orifice and pressure indicator	$\sqrt{I\left(\frac{P_3}{P_{std}}\right)\left(\frac{298}{T_3}\right)}$	$\sqrt{I}$
Rotameter, or orifice and pressure recorder having a square root scale*	$\sqrt{I\left(\frac{P_3}{P_{std}}\right)\left(\frac{298}{T_3}\right)}$	I

*This scale is recognizable by its non-uniform divisions and is the most commonly available for high-volume samplers.

After the initial and final sampling standard flow rates have been determined, calculate the average sampling standard flow rate (Q_{std}) using the following equation:

(Eq. 5-4)
$$Q_{std} = \frac{Q_I + Q_F}{2}$$

Where: Q_{std} = *standard volumetric flow rate, std* m^3/min

Q_I = *initial sampling standard flow rate, std* m^3/min

Q_F = *final sampling standard flow rate, std* m^3/min

22. Calculate the total air volume sampled using the following equation:

(Eq. 5-5)

$$V_{std} = Q_{std} \times t$$

Where: V_{std} = *total air volume sampled, std* m^3

Q_{std} = *average sampling standard flow rate, std* m^3/min

t = *sampling time, min*

23. Calculate and report the particulate matter concentration using the following equation:

(Eq. 5-6)

$$TSP_{std} = \frac{(W_f - W_i)10^6}{V_{std}}$$

Where: TSP_{std} = *mass concentration of total suspended particulate matter,* $\mu g/std\ m^3$

W_i = *initial weight of clean filter, g*

W_f = *final weight of exposed filter, g*

V_{std} = *air volume sampled, std* m^3

10^6 = *conversion of g to* μg

24. If desired, the actual particulate matter concentration can be calculated as follows:

(Eq. 5-7)

$$(TSP)_{act} = TSP_{std}(P_{act}/P_{std})(T_{std}/T_{act})$$

Where: $(TSP)_{act}$ = *actual concentration at field conditions,* $\mu g/m^3$

TSP_{std} = *concentration at standard conditions,* $\mu g/std\ m^3$

P_{act} = *average barometric pressure at the field during sampling period, mm Hg*

P_{std} = *760 mm Hg (or 101 kPa)*

T_{act} = *average ambient temperature at the field during the sampling period, K*

T_{std} = *298 K*

In 1987, EPA abolished the National Ambient Air Quality Standard (NAAQS) for total suspended particulate matter and established a particulate matter standard for PM_{10}. Determining compliance with the new PM_{10} standard required use of a reference or equivalent method for PM_{10}. As a result, the high-volume sampler FRM was no longer used to determine compliance with EPA's particulate matter standard. However, the high-volume sampler FRM remains as the reference sampling method for determining compliance with the lead NAAQS and sampling for subsequent analysis for other inorganic compounds in SPM.

Sample Problems

Problem 1: High-Volume Sampling

Determine the total suspended particulate matter (TSP) concentration at actual sampling conditions from the following sampling and analysis data.

Mass of filter before sampling: 3.182 g
Mass of filter after sampling: 3.455 g
Ambient temperature: 20° C or 293 K
Ambient pressure: 740 mm Hg
Starting flow rate: 1.70 m^3/min
Ending flow rate: 1.41 m^3/min
Sampling period (*t*): 24 hours

Solution:

$$Q_{act} = \text{Average sampling flow rate at field sampling conditions}$$

$$= \frac{\text{Initial actual flow rate} + \text{Final actual flow rate}}{2}$$

$$Q_{act} = \frac{1.70\,\text{m}^3/\text{min} + 1.41\,\text{m}^3/\text{min}}{2} = 1.555\,\text{m}^3/\text{min}$$

$$V_{act} = Q_{act} \times t$$

$$V_{act} = 1.555\,\mathrm{m}^3/\mathrm{min}\,(24\mathrm{hr})(60\,\mathrm{min/hr}) = 2239.2\,\mathrm{m}^3$$

$$\text{Mass of TSP collected} = 3.455\mathrm{g} - 3.182\mathrm{g} = 0.273\mathrm{g}\,(10^6\,\mu\mathrm{g/g}) = 273{,}000\mu\mathrm{g}$$

TSP_{act} concentration = Mass of TSP/V_{act}

$$TSP_{act} = 273{,}000\mu\mathrm{g}\ /2239.2\mathrm{m}^3$$

$$\text{TSP concentration} = 122\,\mu\mathrm{g/m}^3$$

Problem 2: High-Volume Sampling

What is the TSP concentration at standard conditions?

Solution:

Correct the concentration to Standard Conditions:

$$TSP_{std} = TSP_{act}\,(P_{std}/P_{act})(T_{act}/T_{std})$$

$$TSP_{std} = 122\,\mu\mathrm{g/m}^3\,(760\,\mathrm{mm}/740\,\mathrm{mm})(293\,\mathrm{K}/298\,\mathrm{K})$$
$$TSP_{std} = 123\mu\mathrm{g/m}^3$$

Or correct the volume to Standard Conditions:

TSP $\text{Concentration}_{std}$ = Mass of TSP collected/V_{std}

$V_{std} = V_{act}\ (P_{act}/P_{std})(T_{std}/T_{act})$

V_{std} = 2239.2m^3(740 mmHg/760 mm Hg)(298K/293K)

V_{std} = 2217.48 m^3

TSP $\text{Concentration}_{std}$ = 273,000 μg/2217.48 m^3 = 123 μg/m^3

Problem 3: High-Volume Sampling

The initial standard flow rate of a high-volume total suspended particulate (TSP) matter sampler was 38 ft^3/min and the final flow rate was 36 ft^3/min. The sampling period was 23 hours and the atmospheric pressure was 740 mm Hg and 20° C. The weight of the filter before sampling was 4.5550 g and the weight after sampling was 4.6850 g. What is the TSP concentration in μg/m^3 at standard conditions of 760 mm Hg and 25° C? Note that 1 m^3/min is equal to 35.3144 ft^3/min.

Solution:

$$\text{Sampling time (t)} = 23\,\text{hrs} \times 60\,\text{min/hr} = 1{,}380\,\text{min}$$

$$Q_{act} = \text{average flow rateat field sampling conditions}$$

$$Q_{act} = \frac{38\frac{\text{ft}^3}{\text{min}} + 36\frac{\text{ft}^3}{\text{min}}}{2} = \frac{37\,\text{ft}^3}{\text{min}}$$

$$Q_{act} = 37\frac{\text{ft}^3}{\text{min}} \times \frac{1\,\text{m}^3}{35.3144\text{ft}^3} = 1.05\,\text{m}^3/\text{min}$$

$$\text{Total Mass} = \text{Final weight} - \text{initial}\left(\text{tare}\right)\text{weight}$$

$$\text{Total Mass}(\mu\text{g}) = (4.6850\text{g} - 4.5550\text{g}) \times 10^6\,\frac{\mu\text{g}}{\text{g}} = 130{,}000\mu\text{g}$$

$$V_{act} = Q_{act} \times t$$

$$V_{act} = 1.05\frac{\text{m}^3}{\text{min}} \times 1{,}380\,\text{min} = 1{,}449\text{m}^3$$

$$V_{std} = V_{act}\left(P_{act}/P_{std}\right)\left(T_{std}/T_{act}\right)$$

$$V_{std} = 1{,}449\text{m}^3\left(\frac{740\,\text{mm}}{760\,\text{mm}}\right)\left(\frac{298\,\text{K}}{293\,\text{K}}\right) = 1{,}435\text{m}^3$$

$$\text{TSP}_{std}\ \text{concentration} = \text{Total Mass}/V_{std}$$

$$\text{TSP}_{std}\ \text{concentration} = \frac{130{,}000\mu\text{g}}{1{,}435\text{m}^3} = 90.59\mu\text{g/m}^3\ \text{or}\ 90.6\mu\text{g/m}^3$$

Analysis of High-Volume Filters

Filters from hi-vol samplers can be analyzed much more thoroughly than by just simple mass concentration determination. After a filter has been weighed, it can be cut into sections for subsequent analysis. Destructive extraction techniques that might be used in preparing the filter for analysis are organic solvent extraction, acid extraction, and aqueous extraction. To determine the amount of organic aerosol present in the ambient air, organics on a portion of a filter can be extracted with an organic solvent, such as chloroform, in conjunction with a Soxhlet ® extractor. The resulting organic fraction can then be analyzed by appropriate techniques, such as infrared or ultraviolet spectrometry. Metals can be extracted from the particulate matter of a portion of a high-volume filter by placing the filter portion in an acid solution. Any filter matter that disintegrates in the acid can be removed by centrifugation. After extraction, the resulting soluble metal solution can be analyzed by a number of methods, including atomic absorption spectrophotometry, atomic emission spectroscopy, polarography, and inductively coupled plasma emission spectroscopy. Water-soluble species (such as sulfates and nitrates) of the particulate matter of a high-volume filter can be extracted using deionized, distilled water. The resulting solution can then be analyzed using methods such as ultraviolet or visible spectrometry.

Sometimes it is necessary that the filter remain intact after analysis. Nondestructive analytical techniques, such as neutron activation x-ray fluorescence, and electron or optical microscopy, can be used in these cases.

The above-mentioned analyses are not required for all filters. Therefore, it must be carefully decided what analyses should be performed on individual filters.

Sampling Accuracy and Precision

The limits of accuracy and precision of any sampling method must be understood for proper interpretation of data obtained using that method. Factors influencing the accuracy and precision of high-volume sampling include sampler operating characteristics, accuracy of calibration, filter characteristics, location of sampler, nature and concentration of particulate matter and gases in the air being sampled, and the humidity of the air.

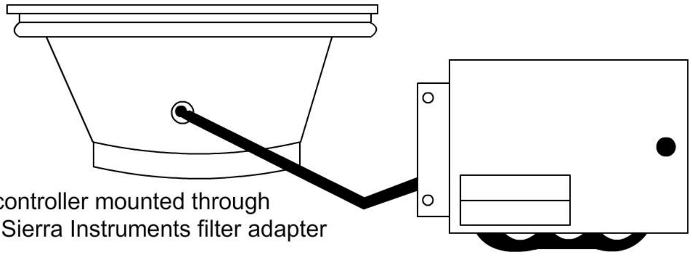
Accuracy

As defined in Section 3 of Appendix A of 40 CFR Part 58, accuracy is the degree of agreement between an observed value and an accepted reference value. It includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations. The accuracy of the particulate measurements can be affected by several known inherent sources of error in the sampling of particulate matter. These include airflow variation, air volume measurement, loss of volatiles, artifacts, humidity, filter handling, and non-sampled particulate matter.

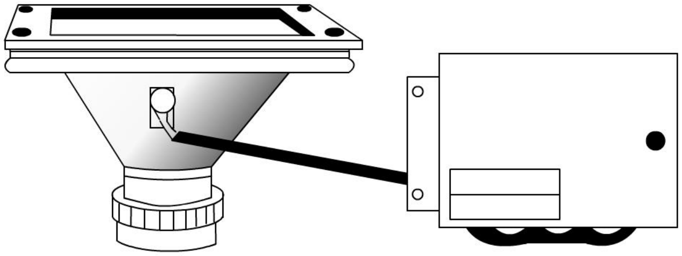
Airflow Variation

The weight of material collected on the filter represents the integrated sum of the product of the instantaneous flow rate times the instantaneous particle concentration. Therefore, dividing this weight by the average flow rate over the sampling period yields the true particulate matter concentration only when the flow rate is constant over the period. The error resulting from a non-constant flow rate depends on the magnitude of the instantaneous changes in the flow rate and in the particulate matter concentration. Normally, such errors are not large, but they can be greatly reduced by equipping the sampler with an automatic flow controlling mechanism that maintains constant flow during the sampling period.

The most popular method of constant flow rate regulation uses a constant temperature thermal anemometer sensor to measure mass flow in the throat of the high-volume sampler's filter adapter (sampling head). Electronic feedback circuitry adjusts the sampler's motor speed to maintain a constant mass flow. Since mass flow is controlled, the volumetric flow rate can be maintained at standard conditions. Thus, flow variations caused by temperature, pressure, line voltage, and particulate matter loading are all compensated for by this system. The system can be retro-fitted to any high-volume sampler (Figure 5-13).



Flowcontroller mounted through
the side of Sierra Instruments filter adapter



Flowcontroller mounted through
the side of GMW filter adapter

Figure 5-13. Constant flow controllers.

Air Volume Measurement

If the flow rate changes substantially or non-uniformly during the sampling period, appreciable error in the estimated air volume may result from using the average of the pre-sampling and post-sampling flow rates. Greater air volume measurement accuracy may be achieved by equipping the sampler with a flow controlling mechanism that maintains constant air flow during the sampling period or by using a calibrated, continuous flow rate recording device to record the actual flow rate during the sampling period and integrating the flow rate over the period.

A high-volume sampler can be modified to provide a continuous recording of flow rate by installing a fixed orifice in the sampler's motor housing and using a pressure transducer to monitor air flow through the sampler and a chart recorder to record the air flow. Such modified high-volume samplers are commercially available (Figure 5-14).

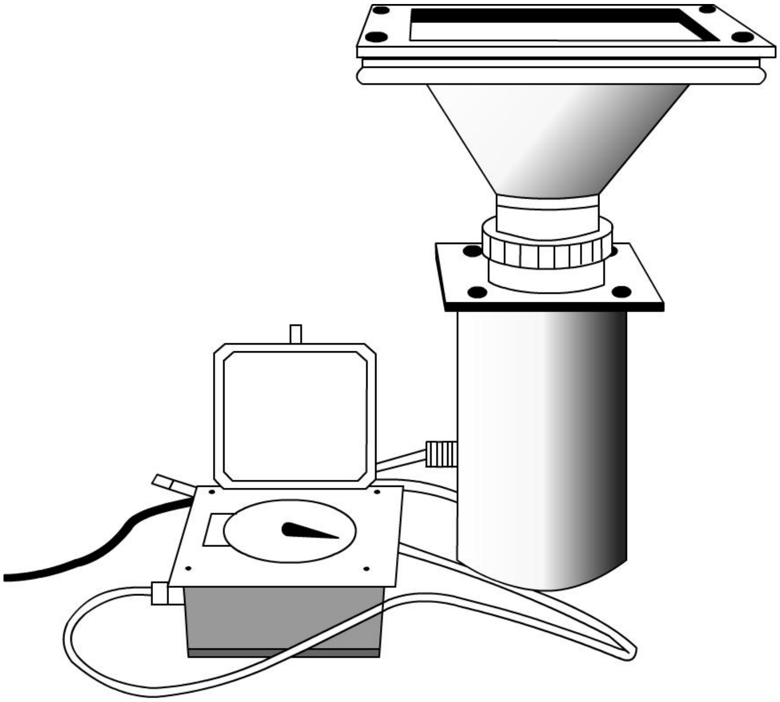


Figure 5-14. Hi-vol sampler modified for continuous recording of flow rate.

Loss of Volatiles

Volatile particles collected on the filter may be lost during subsequent sampling or during shipment and/or storage of the filter prior to the post-sampling weighing. Although such losses are largely unavoidable, the filter should be reweighed as soon after sampling as practical.

Artifact Particulate Matter

Artifact particulate matter can be formed on the surface of alkaline glass fiber filters by oxidation of acid gases in the sample air, resulting in a higher than true TSP determination. This effect usually occurs early in the sampling period and is a function of the filter pH and the presence of acid gases. It is generally believed to account for only a small percentage of the filter weight gain, but the effect may become more significant when relatively small particulate matter weights are encountered.

Humidity

Glass fiber filters are comparatively insensitive to changes in relative humidity, but collected particulate matter can absorb moisture. The moisture conditioning procedure minimizes, but may not completely eliminate, error due to moisture.

Filter Handling

Careful handling of the filter between the pre-sampling and post-sampling weighings is necessary to avoid error due to loss of fibers or particles from the filter. A filter cartridge used to protect the filter can minimize handling errors.

Non-Sampled Particulate Matter

Particulate matter may be deposited on the filter by wind during periods when the sampler is inoperative. Errors from this source can be minimized by using an automatic mechanical device that keeps the filter covered during non-sampling periods (Figure 5-15), or by timely installation and retrieval of filters to minimize the non-sampling periods prior to and following sampler operation.

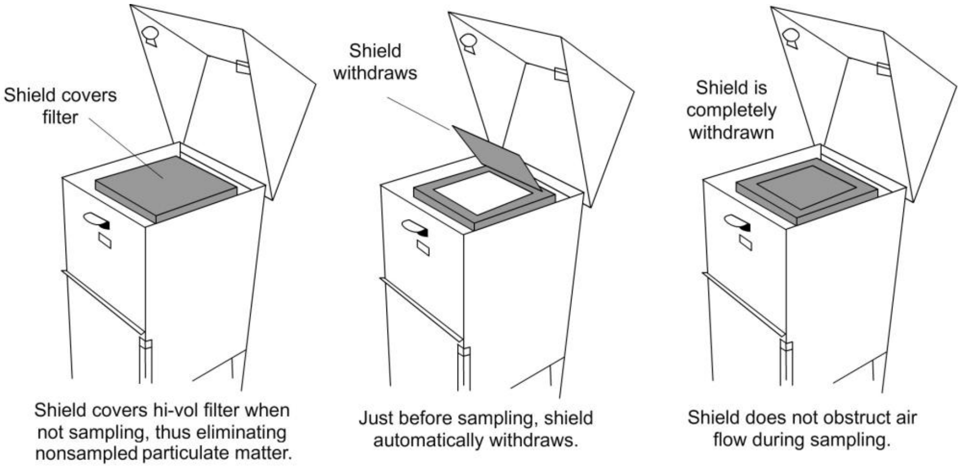


Figure 5-15. Modification for minimizing sampling error caused by nonsampled particulate matter.

Timing Errors

Samplers are normally controlled by clock timers (Figure 5-16a) set to start and stop the sampler at midnight. Errors in the nominal 1440-min sampling period may result from a power interruption during the sampling period or from a discrepancy between the start or stop time recorded on the filter information record and the actual start or stop time of the sampler. Such discrepancies may be caused by poor resolution of the timer set points, timer error due to power interruption, missetting of the timer, or timer malfunction. In general, digital electronic timers have much better set-point resolution than mechanical timers, but require a battery back-up system to maintain continuity of operation after a power interruption. A continuous flow recorder or elapsed time meter (Figure 5-16b) provides an indication of the sampler run-time, as well as indication of any power interruption during the sampling period.

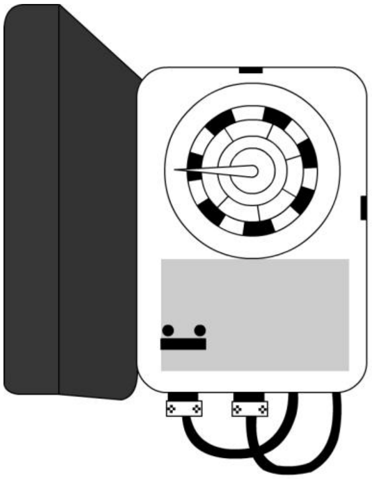


Figure 5-16a. Seven-day mechanical clock timer.

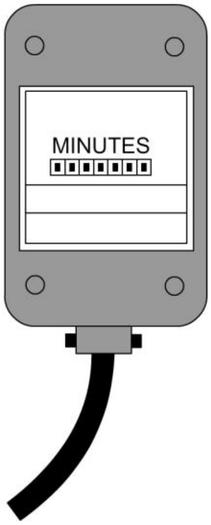


Figure 5-16b. Elapsed time meter.

Recirculation of Sampler Exhaust

Under stagnant wind conditions, sampler exhaust air can be re-sampled. Re-sampling does not appear to affect the TSP measurement substantially, but may result in increased carbon and copper in the collected sample caused by reentrainment of particles from the sampler's motor. This problem can be reduced by ducting the exhaust air well away (at least 40 cm), preferably downwind, from the sampler's air inlet.

Wind Speed and Direction Sensitivity

The rectangular, gabled roof of the high-volume sampler causes the size of the particles collected by the sampler to vary with wind speed and direction.

Independent performance audits should be conducted to estimate the accuracies of the flow rate calibrations of high-volume samplers. A Reference Flow device (ReF device), developed by the National Institute of Science and Technology (NIST) under contract to the U.S. EPA, can be used for the performance audits (Figure 5-17). The ReF device is a modified orifice with five resistance plates that can be mounted directly to the filter adapters of high-volume samplers. The resistance plates are used to produce known flow rates of air through the samplers. However, if high-volume samplers equipped with constant flow controllers are being audited, a clean filter should be used in place of the resistance plates, because resistance plates may cause abnormal flow patterns around the controller flow sensors, thus affecting the performance of the flow controllers.

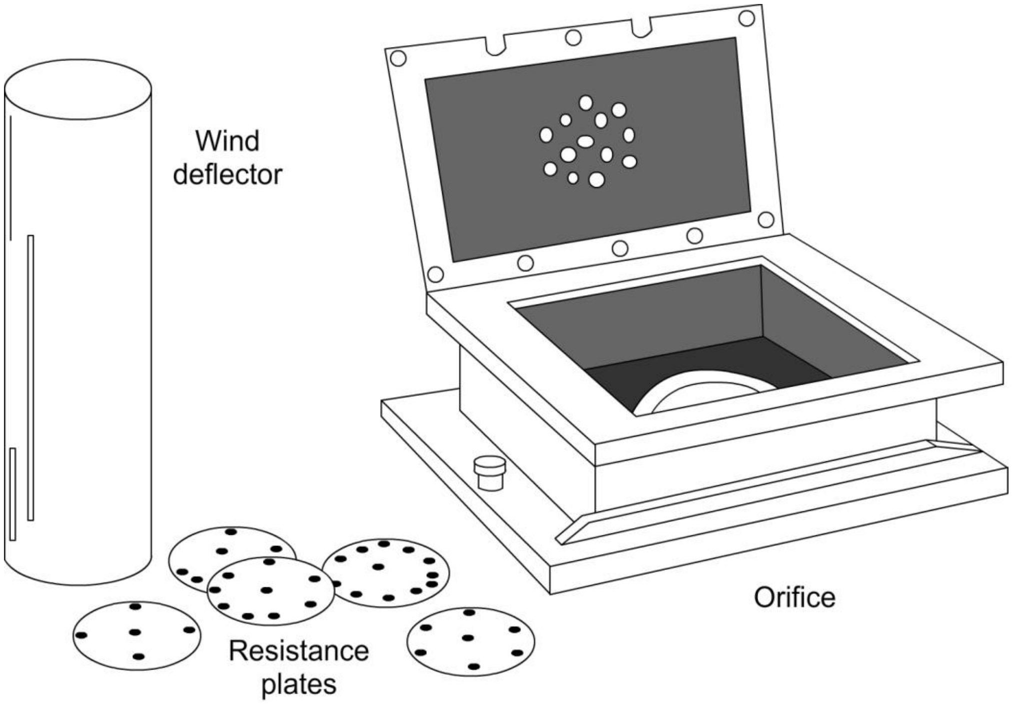


Figure 5-17. U.S. EPA Reference Flow device (ReF device).

Precision

Precision can be defined as the measurement of mutual agreement among individual measurements of the same property, usually under prescribed similar conditions, expressed generally in terms of standard deviation. Collaborative testing has shown that the high-volume sampling method for total suspended particulate matter is capable of achieving a relative standard deviation (coefficient of variation) for single analyst precision (repeatability) of 3.0% and a relative standard deviation for interlaboratory precision (reproducibility) of 3.7%. However, collaborative tests are often performed under ideal conditions. Therefore, collocated samplers should be used to estimate precision under field conditions for high-volume samplers of air monitoring networks.

Maintenance

The high-volume sampler requires less maintenance than most air monitoring instruments, but a certain level of preventive maintenance is needed to ensure dependable operation. The sampler motor maintenance consists of periodic motor brush replacement (if the sampler does not use a brushless motor), usually after 400 to 500 hours of operation at normal line voltage of 115 volts. The life of these brushes can be extended from 400 to 500 hours to approximately 600 to 750 hours by using a "step-down" transformer (Figure 5-18). Worn brushes, if not replaced, will result in damage to the motor. The flow rate measuring device should be cleaned whenever foreign material is detected in the device or the device behaves erratically. The faceplate gasket, which seals the filter to the filter adapter, will deteriorate in time and will need periodic replacement.

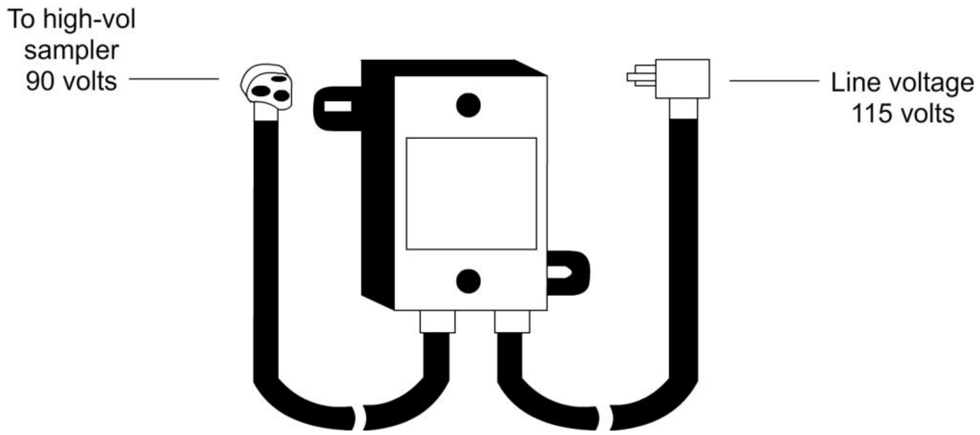


Figure 5-18. "Step-down" transformer.

Deterioration is indicated by indistinct margin patterns around the edge of the filter after sampling. New filters can be secured with rubber contact cement or double-side adhesive tape. There are also two motor gaskets that should be replaced when worn.

Any leaks in the housing should be repaired, especially openings in the roof or in the filter adapter housing. The inside and outside of the shelter must be kept clean and free of accumulated debris, as this material might be drawn onto the filter. Time indicators and 24-hour timers must also be kept operational along with any power cords and electrical connections. Plastic tubing used in the indication of flow rate must also be kept clean.

Samplers must be recalibrated after any major maintenance. This includes replacement of the motor or motor brushes any time the flow rate measuring device is replaced or repaired (including cleaning), or any time tubing is replaced or cleaned. If motor brushes are replaced, the motor must be operated against a flow resistance that is equal to a clean filter for several hours in order to properly seat the brushes against the motor's armature before the sampler can be recalibrated. Table 5-5 summarizes major maintenance activities.

Table 5-5. High-volume sampler maintenance activities.

Equipment	Acceptance Limits	Frequency and method of measurement	Action if requirements are not met
Sampler motor	400 h of motor brush operation; no malfunction	Visually check upon receipt and after every 400 h of operation	Replace motor brushes; other maintenance as indicated
Faceplate gasket	No leaks at the filter seal	Visually check after each sampling period	Replace the gasket
Flow rate measuring device	No foreign materials; stable operation	Visually check for each sample	Clean; replace if damaged

Motor gaskets	Leak-free fit	Visually check after each 400 h of operation	Replace gaskets
Filter adapter (sampling head)	No leaks	Visually check after each 200 h of operation	Replace filter adapter

Summary

Although the high-volume method rarely serves the purpose for which it was originally designed (i.e., determining TSP concentration), it continues to be the method of choice for the determination of lead in SPM. Additionally, the high-volume method is increasingly being used to collect a sample for later analysis for metals (i.e. inorganic particles) as interest in assessing air toxics continues to increase.

5.4 FRM for the Determination of Particulate Matter as PM_{10}

Applicability

The Federal Reference Method (FRM) for PM_{10} described here is provided from Appendices J and M of 40 CFR Part 50. This method provides for the measurement of the mass concentration of particulate matter with an aerodynamic diameter less than or equal to a nominal 10 μm (PM_{10}) in ambient air over a 24-hour period for purposes of determining attainment and maintenance of the primary and secondary national ambient air quality standards for particulate matter. The measurement process is nondestructive, and the PM_{10} sample can be subjected to subsequent physical or chemical analyses. Quality assurance procedures and guidance are provided in 40 CFR Part 58, Appendices A and B, and in Volume II of the QA Handbook. Although this section discusses the Federal Reference Method (FRM) for PM_{10}, Class III (continuous monitors) Federal Equivalent Methods (FEM) have been approved by EPA for time-resolved and 24-hour integrated mass concentrations of PM_{10}. These FEM monitors (Beta Gauge and TEOM®) are discussed in the "Continuous Monitoring for Particulate Matter" section of this chapter.

Principle

In the FRM for PM_{10}, an air sampler draws ambient air at a constant flow rate into a specially shaped inlet where the suspended particulate matter is inertially separated into one or more size fractions within the PM_{10} size range (Figures 5-19 and 5-20). Each size fraction in the PM_{10} size range is then collected on a separate filter over the specified sampling period. The particle size discrimination characteristics (sampling effectiveness and 50% cutpoint) of the sampler inlet are prescribed as performance specifications in 40 CFR Part 53. Two types of samplers that meet EPA FRM designation for PM_{10} requirements are the high-volume (1000 L/min) PM_{10} sampler and the dichotomous sampler (16.7 L/min).

Each filter (or both filters, in the case of the dichotomous sampler) is weighed (after moisture equilibration) before and after use to determine the net weight (mass) gain due to collected PM_{10}. The total volume of air sampled, measured at the actual ambient temperature and pressure, is determined from the measured flow rate and the sampling time. The mass concentration of PM_{10} in the ambient air is computed as the total mass of collected particles in the PM_{10} size range divided by the volume of air sampled, and is expressed in micrograms per cubic meter. This is the mass concentration of the particulate matter present in the sampled air.

A method based on this principle will be considered a FRM if (a) the associated sampler meets the requirements specified in Appendices J and M of 40 CFR Part 50 and requirements in 40 CFR Part 53, and (b) the method has been designated as a FRM in accordance with 40 CFR Part 53.

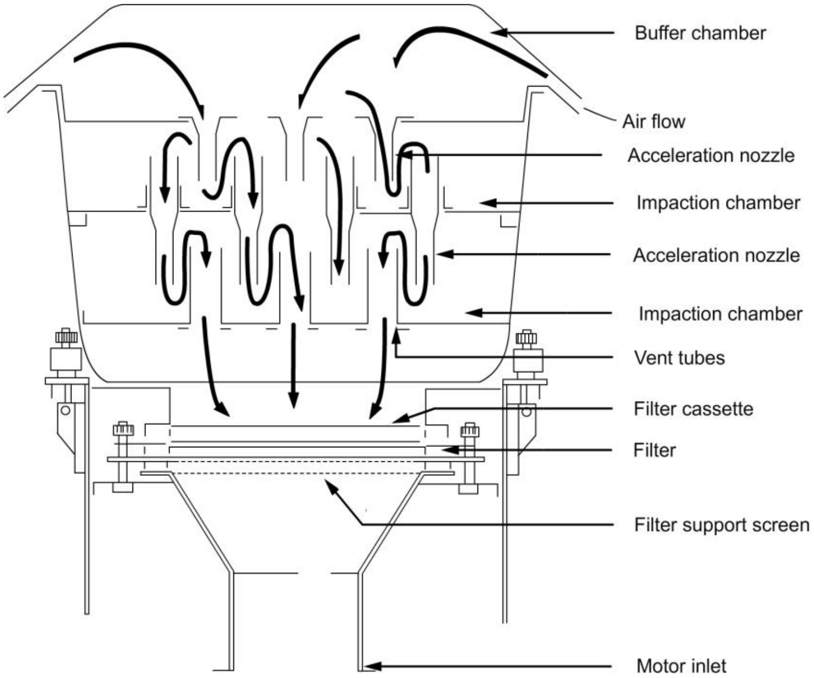


Figure 5-19. Schematic diagram of an impaction inlet.

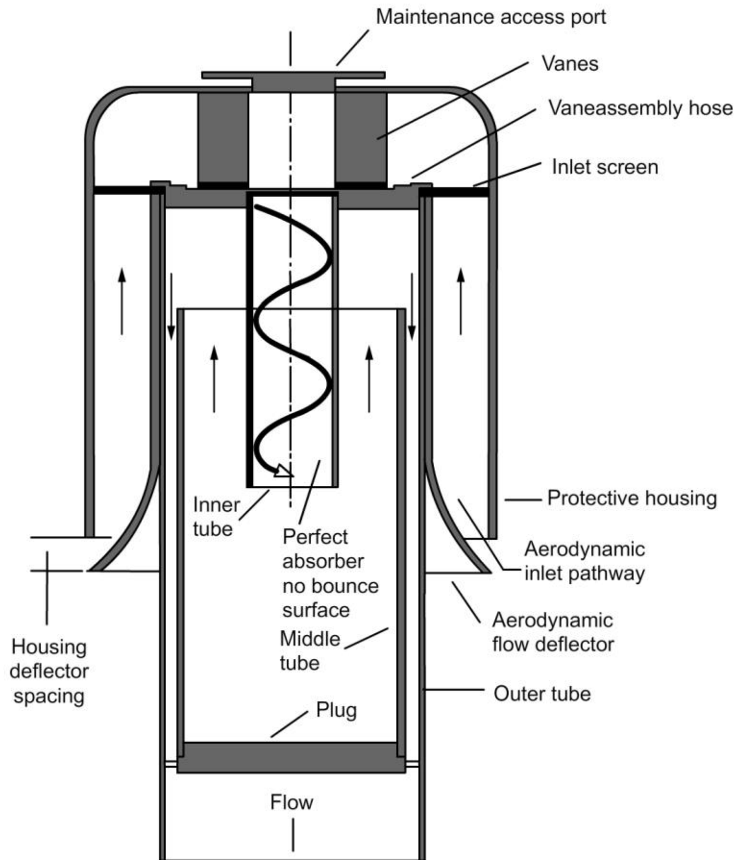


Figure 5-20. Schematic diagram of a cyclonic inlet.

Range

The lower limit of the mass concentration range is determined by the repeatability of filter tare weights, assuming the nominal air sample volume for the sampler. For samplers having an automatic filter-changing mechanism, there may be no upper limit. For samplers that do not have an automatic filter-changing mechanism, the upper limit is determined by the filter mass loading, beyond which the sampler no longer maintains the operating flow rate within specified limits due to increased pressure drop across the loaded filter. This upper limit cannot be specified precisely because it is a complex function of the ambient particle size distribution and type, humidity, filter type, and perhaps other factors. Nevertheless, all samplers should be capable of measuring 24-hour PM_{10} mass concentrations of at least 300 μg/std m^3 while maintaining the operating flow rate within the specified limits.

Precision

SLAMS Measurement System Precision

The majority of air monitoring stations are in State and Local Air Monitoring Stations (SLAMS), which includes National Core (NCore), Photochemical Assessment Monitoring Stations PAMS, and all other state or locally operated stations that have not been designated as Special Purpose Monitoring (SPM) or Prevention of Significant Deterioration (PSD) sites. Appendix A of 40 CFR Part 58 addresses the QA/QC requirements applicable to SLAMS, SPM, and PSD sites.

Appendix A of 40 CFR Part 58 states that all ambient monitoring methods or analyzers used in SLAMS shall be tested periodically to quantitatively assess the quality of the SLAMS data. The terminology used to define the quality or uncertainty of the SLAMS measurements includes precision, accuracy, and bias. Precision is defined as the measurement of mutual agreement among individual measurements of the same property, usually under prescribed similar conditions, expressed generally in terms of the standard deviation. The SLAMS precision goal for PM_{10} is ± 15% (QA Handbook, Volume II, Section 2.011).

Estimates of the precision of SLAMS automated methods for PM_{10} are made based on checks of the operational flow rate of each analyzer using a flow rate transfer standard. These checks must be conducted at least once every 2 weeks. For networks using manual methods for PM_{10}, precision is determined using collocated samplers at selected sites. One of the samplers is designated as the primary sampler whose data will be used to report air quality for the site, and the other sampler is designated as the duplicate sampler. Estimates of the precision are calculated according to the procedures specified in Section 4 of Appendix A of Part 58.

Initial Operational Precision of a FRM Sampler

In addition to the Part 58 precision requirements associated with SLAMS PM_{10} measurements, there are specifications in Appendix J of 40 CFR Part 50 which address the initial operational precision of a candidate FRM sampler. These specifications state that the precision of PM_{10} samplers must be 5 $\mu g/m^3$ for PM_{10} concentrations below 80 $\mu g/m^3$, and 7% for PM_{10} concentrations above 80 $\mu g/m^3$. The detailed and lengthy tests to determine whether or not a candidate sampler complies with the precision specifications are included in 40 CFR Part 53, as are the provisions for EPA designation of reference (FRM) and equivalent (FEM) methods for candidate PM_{10} monitors.

Accuracy

SLAMS Measurement System Accuracy

Appendix A of Part 58 defines accuracy as the degree of agreement between an observed value and an acceptable reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations. The accuracy goal for SLAMS PM_{10} measurements is ± 20% (QA Handbook, Volume II, Section 3.01). The accuracy of automated PM_{10} analyzers is determined by conducting quarterly audits of at least 25% of the SLAMS analyzers so that each analyzer is audited at least once per year. The audit is performed by measuring the analyzer's normal operating flow rate, using a certified flow rate transfer standard. The percent difference between the sampler's indicated flow rate and the transfer standard flow rate is used to calculate accuracy. The procedures are specified in Appendix A of Part 58.

Initial Operational Accuracy of a FRM Sampler

It is difficult to define the absolute accuracy of PM_{10} samplers because of the variation in the size of atmospheric particles and the variation in concentration with particle size. Therefore, 40 CFR Part 53 includes the specification for the sampling effectiveness of PM_{10} samplers that are candidates for reference (FRM) or equivalent method (FEM) designation. This specification requires that the expected mass concentration calculated for a candidate PM_{10} sampler, when sampling a specified particle size distribution, be within ± 10% of that calculated for an ideal sampler whose sampling effectiveness is explicitly specified. In addition, the particle size for 50% sampling effectiveness is required to be 10 ± 0.5 μm. Other accuracy specifications prescribed for reference (FRM) or equivalent method (FEM) designation are related to flow measurement and calibration, filter media, analytical weighing procedures, and artifacts.

Potential Sources of Error

There are a number of possible sources of error in measuring PM_{10} concentration levels in ambient air, including volatile particles, artifacts, humidity, filter handling, flow rate variation, and air volume determination. The FRM also addresses the configuration of the sampler, filter calibration, operational procedure, and concentration calculation.

Volatile Particles

Volatile particles collected on filters are often lost during shipment and/or storage of the filters prior to the postsampling weighing. Although shipment or storage of loaded filters is sometimes unavoidable, filters should be reweighed as soon as practical to minimize these losses. Filters are usually stored and shipped cold in order to prevent volatile losses.

Artifacts

Positive artifacts in PM_{10} concentration measurements can result from absorption or adsorption on filters and collected PM. Common positive artifacts are sulfur dioxide, nitric acid, and organic carbon species. Positive artifacts not only overestimate true PM mass, but they can also change the filter alkalinity. For example, retention of sulfur dioxide on filters, followed by oxidation to sulfate (sulfate formation), is a phenomenon that increases with increasing filter alkalinity. Little or no artifact sulfate formation should occur using filters that meet the alkalinity specification in the FRM in Appendix M of 40 CFR Part 50. Artifact nitrate formation, resulting primarily from retention of nitric acid, occurs to varying degrees on many filter types, including glass fiber, cellulose ester, and many quartz fiber filters. Loss of true atmospheric particulate nitrate during or following sampling may also occur due to dissociation or chemical reaction. This phenomenon has been observed on Teflon® filters and inferred for quartz fiber filters. The magnitude of nitrate artifact errors in PM_{10} mass concentration measurements will vary with location and ambient temperature; however, for most sampling locations, these errors are expected to be small. Glass and quartz fiber filters are especially prone to the adsorption of organic carbonaceous species in the air. Denuders can be used to selectively remove gaseous components of ambient air drawn into the sampler so that only particles are collected on the filter.

A negative artifact occurs when chemical components of PM are lost. Changes in ambient concentrations of gas and particle phase organic components, and in temperature, can alter volatile and semi-volatile species adsorbed onto collected particles. Volatile and semi-volatile components of PM can be lost during temperature increases during sampling and transport, and when sampling at high face velocities. For this reason, PM_{10} filters should be transported cold. The negative artifact associated with filter velocity is considered negligible under typical PM_{10} and $PM_{2.5}$ flow rates. The negative bias related to negative artifacts is typically much less than the bias of positive artifacts for typical ambient conditions, sampling face velocities, and collection times.

Humidity

The effects of ambient humidity on the sample are unavoidable. The filter equilibration procedure in the FRM is designed to minimize the effects of moisture on the filter medium. For this reason, Teflon filters are pre-weighed and post-weighed at controlled temperature and humidity.

Filter Handling

Careful handling of filters between presampling and postsampling weighings is necessary to avoid errors due to damaged filters or loss of collected particles from the filters. Use of a filter cartridge or cassette may reduce the magnitude of these errors.

Flow Rate Variation

Variations in the sampler's operating flow rate may alter the particle size discrimination characteristics of the sampler inlet. The magnitude of this error will depend on the sensitivity of the inlet to variations in flow rate and on the particle distribution in the atmosphere during the sampling period. The use of a flow control device is required to minimize this error.

Air Volume Determination

Errors in the air volume determination may result from errors in the flow rate and/or sampling time measurements. The flow control device serves to minimize errors in the flow rate determination, and an elapsed time meter is required to minimize the error in the sampling time measurement.

PM_{10} Sampler Apparatus

The sampler is designed to:

- draw the air sample into the sampler inlet and through the particle collection filter at a uniform face velocity,
- hold and seal the filter in a horizontal position so that sample air is drawn downward through the filter,

- allow the filter to be installed and removed conveniently,
- protect the filter and sampler from precipitation and prevent insects and other debris from being sampled,
- minimize air leaks that would cause error in the measurement of the air volume passing through the filter,
- discharge exhaust air at a sufficient distance from the sampler inlet to minimize the sampling of exhaust air, and
- minimize the collection of dust from the supporting surface.

Filter Media

No commercially available filter medium is ideal in all respects for all PM_{10} samplers. In addition to the user's goal of determining concentration, other factors such as cost, ease of handling, and physical and chemical characteristics all contribute to the specific filter chosen for sampling. In addition to those factors, certain types of filters may not be suitable for use with some samplers, particularly under heavy loading conditions (high mass concentrations), because of high or rapid increase in the filter flow resistance that would exceed the capability of the sampler's flow control device. However, samplers equipped with automatic filter-changing mechanisms may allow the use of these types of filters.

Filter specifications are provided in the FRM and address collection efficiency, integrity, and alkalinity. The filter medium collection efficiency must be greater than 99% as measured by the dioctyl phthalate (DOP) test, American Society of Testing Materials (ASTM) 2986.

The filter conditioning environment must control the temperature to ± 3°C and the relative humidity to ± 5%. Other topics covered in the FRM include the analytical balance calibration procedure, sampler operational procedure, and sample maintenance.

Calculations

Calculate the total volume of air sampled as:

(Eq. 5-8)

$$V_{act} = Q_a t$$

Where:

V_{act} = *total air sampled at ambient temperature and pressure,* m^3

Q_a = *average sample flow rate at ambient temperature and pressure,* m^3/min

t = *sampling time, min*

Calculate the PM_{10} concentration as:

(Eq. 5-9)

$$PM_{10} = \left(\frac{(W_f - W_i) x 10^6}{V_{std}} \right)$$

Where: PM_{10} = *mass concentration of* PM_{10}, *μg/*m^3
W_f, W_i = *final and initial weights of filter collecting* PM_{10} *particles, in g*
10^6 = *conversion of g to μg (use* 10^3 *to convert mg to μg)*
V_{std} = *volume at EPA standard temperature and pressure*

Note: If more than one size fraction in the PM_{10} size range is collected by the sampler, the sum of the net weight gain by each collection filter $[\sum(W_f - W_i)]$ is used to calculate the PM_{10} mass concentration.

Sample Problems

Problem 1: PM_{10} *Sampling*

A dichotomous sampler was used for measuring PM_{10} concentrations in the atmosphere. Two filter weights were obtained: one for fine particulates and one for coarse particulates. In measuring PM_{10} concentrations with a dichotomous sampler, the two filter weights are combined to determine the PM_{10} concentrations. In this sampling situation, the final gross weight of the fine particles was 101.080 mg with a tare weight of 100.100 mg. The final gross weight of the coarse particles was 104.100 mg with a tare weight of 103.175. The average flow rate for the 23-hour sampling period was 16.80 L/min. The average atmospheric pressure was 745 mm Hg, and the average temperature was 23.5° C. What is the PM_{10} concentration for this sample required as μg/m^3 at actual atmospheric concentration?

Solution:

Sampling (t) = 23 hrs × 60 min/hr = 1,380 min

$V_{act} = Q_{act} \text{ x } t$

$V_{act} = 16.8 \text{ L/min} \times 1{,}380 \text{ min} = 23{,}184 \text{ L} \times \text{m}^3/1000\text{L} = 23.18 \text{ m}^3$

$$PM_{10} = \frac{(W_f - W_i) \times 10^6}{V_{act}}$$

Where: W_f = mass in μg

W_i = mass in μg

V_{act} = volume in m^3, at actual temperature and pressure

10^6 = conversion factor from g to μg

In this problem:

$$PM_{10} = \frac{\left[\left(W_{f\_PM2.5} - W_{i\_PM2.5}\right) + \left(W_{f\_PM10-PM2.5} - W_{i\_PM10-PM2.5}\right)\right] \times 10^3}{V_{act}}$$

Where: 10^3 = conversion factor from mg to μg

$$PM_{10} = \frac{\left[(101.080\text{mg} - 100.100\text{mg}) + (104.100\text{mg} - 103.175\text{mg})\right] \times \frac{10^3\,\mu\text{g}}{\text{mg}}}{V_{act}}$$

Mass = Final weight - initial (tare) weight

Mass of fine particles = 101.080 mg - 100.100 mg = 0.98 mg × 10^3 μg/mg

Mass of fine particles = 980 μg

Mass of coarse particles = 104.100 mg - 103.175 mg = 0.925 mg × 10^3 μg/mg
= 925 μg
Total mass of particles = 980 μg + 925 μg = 1,905 μg

PM_{10} Concentration$_{act}$ = total mass of particles/V_{act} = 1,905 μg/ 23.18 m^3
= 82.18 μg/m^3 or 82.2 μg/m^3

Problem 2: PM_{10} Sampling

The gross weight of the fine particulate filter from a PM_{10} dichotomous sampler was 0.990660 g with a tare weight of 0.990100 g. The gross weight and tare weight of the coarse particulate filter were the same as the fines. The total volume sampled at actual atmospheric conditions of 750 mm Hg and 23° C was 24,330 L. What is the calculated PM_{10} concentration in μg/m^3 at actual atmospheric conditions?

Solution:

V_{act} = 24,330 L × m^3/1000 L = 24.33 m^3

$$PM_{10} = \frac{\left(W_f - W_i\right) \times 10^6}{V_{act}}$$

Where: W_f = mass in μg

W_i = mass in μg

V_{act} = volume in m^3, at actual temperature and pressure

10^6 = conversion factor from g to µg

$$PM_{10} = \frac{2\,(0.990660\text{g} - 0.990100\text{g}) \times 10^6}{(24{,}330\text{L})\,(\text{m}^3 / 1000\,\text{L})} = \frac{1120\,\text{mg}}{24.33\,\text{m}^3} = 46.03\,\mu\text{g/m}^3$$

Mass = Final weight - initial (tare) weight

Mass fine particles = 0.990660 g - 0.990100 g = 0.000560 g

Mass fine particles = 0.000560 × 10^6 µg/g = 560 µg

Mass of coarse particles is the same as fine particles, or 560 µg

Total mass of fine and coarse = 1,120 µg

PM_{10} Concentration$_{act}$ = Total mass of fine and coarse/V_{act}

PM_{10} Concentration$_{act}$ = 1,120 µg/24.33 m^3 = 46.03 µg/m^3 or 46.0 µg/m^3

5.5 FRM and FEM for the Determination of Fine Particulate Matter as $PM_{2.5}$

Several samplers have been approved by EPA as FRM and FEM samplers for $PM_{2.5}$. Although FRM samplers have been used extensively at monitoring sites, some FEM samplers can provide a higher level of convenience and mass concentration information than traditional FRM samplers. Specific Class designations of FEM samplers are based on the degree of deviation from FRM samplers. This section highlights the operation of the FRM sampler, and explains the general differences between FRM and FEM samplers.

Reference Methods for $PM_{2.5}$ (FRM)

The FRM sampler measures the mass concentration of fine particulate matter, having an aerodynamic diameter less than or equal to 2.5 µm ($PM_{2.5}$), in ambient air over a 24-hour period. The measurements provide data to determine whether the primary and secondary national ambient air quality standards for fine particulate matter are met. The measurement process is considered to be nondestructive, and the $PM_{2.5}$ sample obtained can be subjected to subsequent physical or chemical analyses. Quality assessment procedures are provided in Part 58, Appendix A of 40 CFR. Specific details on Federal Reference Method (FRM) sampling for $PM_{2.5}$ can be found in Appendix L 40 CFR Part 50.

Principle

An electrically powered air sampler draws a 24-hour ambient air sample at a constant volumetric flow rate into a specially shaped inlet (Figure 5-21) and through an inertial particle size separator (WINS Impactor or Very Sharp Cut Cyclone). The suspended particulate matter in the $PM_{2.5}$ size range is separated from the larger particles (Figure 5-22) and then collected on a polytetrafluoroethylene (PTFE) filter. Each filter is weighed (after moisture and temperature conditioning) before and after sample collection to determine the net gain in weight of $PM_{2.5}$. The total volume of air sampled at actual temperature and pressure conditions is calculated from the measured flow rate and sampling time. The mass concentration of $PM_{2.5}$ collected, in micrograms per cubic meter ($\mu g/m^3$), is calculated by dividing the net gain in weight by the total volume of air sampled.

Measurement Range

Lower Concentration Limit. The lower detection limit of the mass concentration measurement range is estimated to be approximately 2 $\mu g/m^3$, based on noted mass changes in field blanks in conjunction with the 24 m^3 nominal total air sample volume specified for the 24-hour sample.

Upper Concentration Limit. The upper limit of the mass concentration range is determined by the filter mass loading, beyond which the sampler can no longer maintain the operating flow rate within specified limits (10% of 16.67 L) due to increased pressure drop across the loaded filter. This upper limit cannot be specified precisely because it is a complex function of the ambient particle size distribution and type, humidity, the individual filter used, the capacity of the sampler flow rate control system, and perhaps other factors. Nevertheless, all samplers are estimated to be capable of measuring 24-hour $PM_{2.5}$ mass concentrations of at least 200 μg/m3 while maintaining the operating flow rate within the specified limits.

Sample Period. The required sample period for $PM_{2.5}$ concentration measurements by this method is 1380 to 1500 minutes (23 to 25 hours).

Precision

SLAMS Measurement System Precision. As stated in Appendix A of 40 CFR 58, precision is defined as the measurement of mutual agreement among individual measurements of the same property, usually under prescribed similar conditions, expressed generally in terms of the standard deviation. A data quality objective of 10% coefficient of variation (CV) or better has been established for the SLAMS operational precision of $PM_{2.5}$ monitoring data.

Precision Measurements Using Collocated Procedures for Automated and Manual Methods of $PM_{2.5}$. Appendix A of 40 CFR 58 describes the requirements for measuring the precision of automated and manual methods for $PM_{2.5}$ using collocated samplers. The requirements include: (1) SLAMS operators must report the number or percent of collocated samplers per reporting organization, (2) an EPA FRM must be collocated with a monitor having the same EPA FRM designation, (3) for monitors designated as an EPA FEM, 50% of the designated monitors shall be collocated with a monitor having the same designation and 50% shall be collocated with an FRM monitor, and (4) during the initial deployment of the SLAMS network, collocated sites should be in areas likely to be in violation of the NAAQS.

For each pair of collocated samplers at the selected sites, one of the samplers is designated as the primary sampler for the site, and the other sampler is designated as the duplicate sampler. The duplicate sampler must be operated concurrently with the primary sampler and on a one-in-six day sampling schedule. Estimates of the precision are calculated using the procedures specified in Appendix A of Part 58.

Initial Operational Precision of a FRM Sampler. In addition to the requirements associated with SLAMS $PM_{2.5}$ precision measurements, there are tests in Section 53.58 of 40 CFR Part 53 which are intended to determine the operational precision of candidate $PM_{2.5}$ samplers during a minimum of 10 days of field operation using three collocated test samplers. In this section, precision is defined as the standard deviation or relative standard deviation of a set of $PM_{2.5}$ measurements obtained concurrently with three or more collocated samplers in actual ambient air field operation. Calculations to determine whether or not the candidate method passes the precision test are specified.

Accuracy and Bias

SLAMS Measurement System Accuracy and Bias. Appendix A of Part 58 defines accuracy as the degree of agreement between an observed value and an acceptable reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components that are due to sampling and analytical operations. An accuracy goal for the $PM_{2.5}$ sampler's flow rate has been specified in Section 2.12 of the QA Handbook, Vol. II, Part II. The goal for accuracy of the sampler flow rate is to be within ± 2% of the value indicated by the audit device (during multipoint verification/calibration), or ± 4% (during one-point verification checks and audits), and to be within ± 2% of the sampler's design flow rate of 16.67 L/min (40 CFR Part 50, Appendix L).

Automated Flow Check Accuracy. Flow rate accuracy in SLAMS automated methods (FEM) for $PM_{2.5}$ is based on checks of the operational flow rate of each analyzer using a certified flow rate transfer standard. These checks must be conducted at least once every 2 weeks, and a randomization with respect to time of day, day of week, and routine service and adjustments is encouraged. An alternative procedure that does not use an external flow rate transfer standard is permissible to obtain the flow rate data from the analyzer's internal flow meter. This alternative procedure is allowed if several conditions are met, one of which requires the flow meter to be audited with an external flow rate transfer standard at least every six months. Details on both procedures can be found in Appendix

A of 40 CFR Part 58. For either procedure, the difference between the flow rate transfer standard and the indicated flow rate of the sampler is used to assess the accuracy of the flow rate using the calculation procedures contained in 40 CFR Part 58, Appendix A.

Manual Flow Check Accuracy. For networks using manual sampling methods for $PM_{2.5}$, the accuracy of the sampler's flow rate is determined by auditing the flow rate of each SLAMS sampler each calendar quarter. A certified flow rate transfer standard is used for the audit. The audit flow rate and the indicated flow rate of the sampler are reported and the difference between the two is used to calculate the flow rate accuracy. Like automated methods, a flow rate audit must be performed every six months by a trained experienced technician other than the routine site operator. Additional information on flow check requirements of manual FRM methods can be found in 40 CFR Part 58, Appendix A.

Initial Operational Accuracy of a FRM Sampler. It is difficult to define the absolute accuracy of $PM_{2.5}$ samplers because of the variation in the size of atmospheric particles and the variation in concentration with particle size. Therefore, 40 CFR Part 53 includes the specification for the sampling effectiveness of $PM_{2.5}$ samplers that are candidates for reference or equivalent method designation. Other specifications for reference or equivalent method designation related to accuracy apply to flow measurement and calibration, filter media, analytical weighing procedures, and artifacts.

Measurement System Bias. Bias is defined as the systematic or persistent distortion of a measurement process that causes errors in one direction. The measurement system bias goal is to be within ± 10% of the measurement obtained by an independent sampler audit. The sampler bias is assessed from the results of an independent FRM performance evaluation to be administered through the EPA Regional Offices. More details on these requirements are contained in the QA Handbook, Vol. II, Part II, Section 2.12, Subsection 13.3.

Filter for $PM_{2.5}$ Sample Collection

The filters specified in the FRM for $PM_{2.5}$ are 46.2 mm diameter filters of polytetrafluoroethylene (PTFE Teflon®), with an integral support ring made of polymethylpentene (PMP) or equivalent inert material. In addition to the type of filter material and support ring, the method includes other filter specifications such as pore size, filter thickness, maximum pressure drop, and filter weight stability.

Although not required for determination of $PM_{2.5}$ mass concentration under this FRM, additional specifications for the filter must be developed by users who intend to subject $PM_{2.5}$ filter samples to subsequent chemical analysis. These supplemental specifications include background chemical contamination of the filter and any other filter parameters that may be required by the method of chemical analysis. All such supplemental filter specifications must be compatible with and secondary to the primary filter specifications.

$PM_{2.5}$ Sampler Configuration

The sampler consists of a sample air inlet, downtube, particle size separator (impactor), filter holder assembly, air pump, flow rate control system, and a flow rate measurement device. An example of the $PM_{2.5}$ inlet is shown in Figure 5-23. Other required components include an ambient and filter temperature monitoring system, barometric pressure measurement system, timer, outdoor environmental enclosure, and suitable mechanical, electrical, or electronic control capabilities to meet or exceed the design and functional requirements specified in the FRM.

The sampler is specified by a combination of design and performance requirements. The components explicitly specified by design are the sample inlet, downtube, particle size separator, filter cassette, and the internal configuration of the filter holder assembly. All other aspects of the sampler are specified in terms of operational function and performance. The design of these other aspects, however, is optional, subject to acceptable operational performance. The test procedures to demonstrate compliance with the design and performance requirements are contained in Subpart E of 40 CFR Part 53.

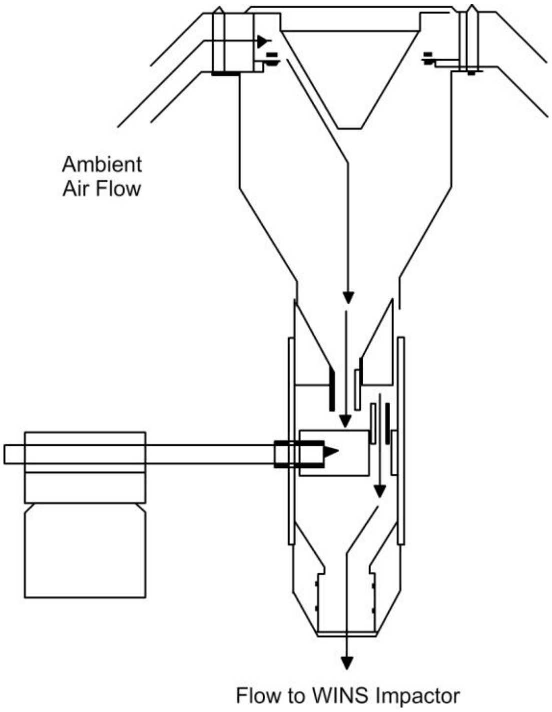


Figure 5-23. Schematic of $PM_{2.5}$ ambient air sampler inlet.

Designated Methods for $PM_{2.5}$

Several samplers have been approved by EPA as Federal Reference Methods (FRM) for the sampling of $PM_{2.5}$.

The "List of Designated Reference and Equivalent Methods" is updated as necessary to reflect any new designations or any cancellation of a designation in effect. This list can be obtained at EPA's Ambient Monitoring Technology

Information (AMTIC) webpage (http://www.epa.gov/ttn/amtic) or at http://www.epa.gov/ttn/amtic/files/ambient/criteria/reference-equivalent-methods-list.pdf.

Equivalent Methods for $PM_{2.5}$ (FEM)

Equivalent methods for $PM_{2.5}$ have a much wider latitude in their design, configuration, and operating principle than FRMs. These methods are not required to be based on filter collection of $PM_{2.5}$; therefore, continuous or semicontinuous analyzers and new types of $PM_{2.5}$ measurement technologies are not precluded as possible equivalent methods. Equivalent methods are not necessarily required to meet all the requirements specified for FRMs, but they must demonstrate both comparability to FRM measurements and similar $PM_{2.5}$ measurement precision.

The requirements that some (but not all) candidate methods must meet for designation as equivalent methods by EPA are specified in 40 CFR Part 53. Three classes of equivalent methods have been established in the 40 CFR Part 53 regulations, based on the degree to which a candidate method deviates from the FRM requirements. All three classes of equivalent methods are acceptable for SLAMS or SLAMS-related $PM_{2.5}$ monitoring. However, not all types of equivalent methods may be equally suited to specific $PM_{2.5}$ monitoring requirements or applications.

A Class I equivalent method means an equivalent method for $PM_{2.5}$ or $PM_{10-2.5}$ which is based on a sampler that is very similar to the sampler specified for reference methods in Appendix L or Appendix O (as applicable) of 40 CFR Part 50, with only minor deviations or modifications, as determined by EPA. For $PM_{2.5}$, Class I equivalent methods are based on samplers that have minor deviations from the specifications for FRM samplers. However, they must meet the 40 CFR Part 53 tests and other requirements that are applicable to FRM samplers. Also, they must be tested to make sure that the modifications of the candidate Class I equivalent method sampler do not significantly compromise sampler performance. Finally, they must be tested for possible loss of $PM_{2.5}$ in any new or modified components in the sampler inlet upstream of the sampler filter.

A Class II equivalent method means an equivalent method for $PM_{2.5}$ or $PM_{10-2.5}$ that utilizes a $PM_{2.5}$ sampler or $PM_{10-2.5}$ sampler in which integrated $PM_{2.5}$ samples or $PM_{10-2.5}$ samples are obtained from the atmosphere by filtration and subjected to a subsequent filter conditioning process followed by a gravimetric mass determination. However, this method is not a Class I equivalent method because of substantial deviations from the design specifications of the sampler specified for reference methods in Appendix L or Appendix O (as applicable) of 40 CFR Part 50. Basically, Class II equivalent method samplers are filter-collection based methods that will generally have one or more substantial deviations from the design or performance specification of the FRM. For example, they might have a different inlet, particle size separator, volumetric flow rate, filter, or filter face velocity than a FRM sampler. Consequently, more extensive performance testing is required for designation of Class II equivalent methods. For $PM_{2.5}$ and $PM_{10-2.5}$, the procedures for testing physical (design) and performance characteristics of reference methods and Class I and Class II equivalent methods can be found in Subpart E of 40 CFR Part 53. Additional procedures for testing performance characteristics of Class II equivalent methods for $PM_{2.5}$ can be found in Subpart F of 40 CFR Part 53.

A Class III equivalent method means an equivalent method for $PM_{2.5}$ or $PM_{10-2.5}$ that is an analyzer capable of providing $PM_{2.5}$ or $PM_{10-2.5}$ ambient air measurements representative of one-hour or less integrated $PM_{2.5}$ or $PM_{10-2.5}$ concentrations as well as 24-hour measurements determined as, or equivalent to, the mean of 24 one-hour consecutive measurements. Regarding $PM_{2.5}$, Class III equivalent methods essentially cover any $PM_{2.5}$ equivalent method sampler that cannot qualify as reference or Class I or II equivalent methods because of more profound differences from the FRM requirements. This class encompasses $PM_{2.5}$ methods such as continuous or semicontinuous $PM_{2.5}$ analyzers and potential new $PM_{2.5}$ measurement technologies. The requirements for designation as Class III methods are the most extensive, and, because of the wide variety of $PM_{2.5}$ measurement principles that could be employed for candidate Class III equivalent methods, the designation requirements are not explicitly provided in 40 CFR Part 53. For similar reasons, much of the information and guidance in this document may not be applicable to the operation of Class III equivalent methods.

Limitations of $PM_{2.5}$ Reference and Class I Equivalent Methods

There are several conditions or effects that limit the degree to which a $PM_{2.5}$ reference or Class I equivalent method can precisely determine the mass concentration of particulate matter in the atmosphere. One limitation is maintaining the specified ambient air flow rate through the sampling inlet and filter assembly. The flow rate determines the size of the particles that will be collected. The effects of this limitation are minimized by following sampler construction requirements and by employing procedures and checks to ensure the proper flow rate is maintained within close tolerances. Refer to Section 6.0, “Calibration Procedures,” and to Section 8.0, “Field Operation,” of EPA’s QA Handbook Vol. II, Part II, Section 2.12, for guidance.

Another important limitation involves changes in the weight of a collected sample due to mishandling, chemical reactions, and volatilization. Handling procedures, choice of filter media, humidity and temperature control of the filter and sample during collection and subsequent processing, and promptness in weighing the sample following collection all help control filter artifacts. The chemical makeup of the $PM_{2.5}$ particulate matter will vary with sampling location and source. Thus, the magnitude of $PM_{2.5}$ weight changes due to chemical and physical processes will also vary with site location.

Weight loss due to mechanical removal of particles from the filter is minimized by carefully removing the filter, in its cassette, from the sampler, storing the filter/cassette in a protective container during transit to the weighing laboratory, and carefully removing the filter from the cassette, conditioning the filter, and neutralizing the static charge on the filter before weighing. Refer to Section 7.0, “Filter Preparation and Analysis,” of EPA’s QA Handbook Vol. II, Part II, Section 2.12, for guidance. As previously discussed, the choice of an essentially neutral Teflon® media filter as the collecting surface minimizes weight gain which may result from chemical reactions that form particles on the filter surface (positive artifacts) or weight loss that can occur due to the thermal or chemical decomposition or evaporation of volatile or semi-volatile compounds (negative artifacts).

Errors in the gravimetric analysis of samples can also result from the buildup of electrostatic charge on filters during their manufacture or during sampling. This static buildup will interfere with the microbalance weighing, but it can be reduced or eliminated by the use of Poloniom-210 antistatic strips before the weighing process begins.

Approved Regional Methods (ARMs)

Approved Regional Methods (ARMs) are automated, continuous $PM_{2.5}$ instruments approved for use within a state, local, or tribal agency used to meet multiple monitoring objectives such as National Ambient Air Quality Standards (NAAQS) and Air Quality Index (AQI). ARMs are similar to Class III (continuous) FEMs, and allow agencies to optimize their $PM_{2.5}$ network with well-performing continuous methods in FEM Class III testing regions where Class III FEMs may not perform well. Candidate ARM samplers must demonstrate statistical comparability with FRM samplers through field testing at a subset of test sites where the ARM is intended to be used.

Calculations

The $PM_{2.5}$ concentration is calculated as:

(Eq. 5-10)
$$PM_{2.5} = \left(W_f - W_i\right)/V_{act}$$

Where:

$PM_{2.5}$ = *mass concentration of* $PM_{2.5}$*,* $\mu g/m^3$

W_f, W_i = *final and initial weights, respectively of the filter used to collect the* $PM_{2.5}$ *particle sample in* μg

V_{act} = *total air volume sample at actual ambient air conditions as provided by the sampler,* m^3

Sample Problems

Problem 1: PM2.5 Sampling

A $PM_{2.5}$ filter weighed 150.200 mg before sampling and 150.900 mg after sampling. The flow rate at atmospheric conditions of 740 mm Hg and 20° C was 16.5 L/min. The sampling period was 24 hours. What is the $PM_{2.5}$ concentration in $\mu g/m^3$ at standard conditions of 760 mm Hg and 25° C?

Solution:

Mass = Final weight - initial (tare) weight

Mass (μg) = 150.900 mg – 150.200 mg = 0.700 mg × 10^3 $\mu g/mg$ = 700 μg

Sampling time (t) = 24 hrs × 60 min/hr = 1,440 min

$V_{act} = Q_{act} \times t$

$= 16.5\ \text{L/min} \times 1{,}440\ \text{min} = 23{,}760\ \text{L} \times \text{m}^3/1{,}000\text{L} = 23.76\ \text{m}^3$

$\text{PM}_{2.5}$ $\text{concentration}_{act} = 700\ \mu\text{g}/\ 23.76\ \text{m}^3 = 29.46\ \mu\text{g/m}^3$ or $29.5\ \mu\text{g/m}^3$

Correct the volume to Standard Conditions:

$V_{std} = V_{act}\ (P_{act}/P_{std})(T_{std}/T_{act})$

$= 23.76\ \text{m}^3 \times (740\ \text{mm Hg}/760\ \text{mm Hg})\ (298\ \text{K}/293\ \text{K}) = 23.53\ \text{m}^3$

$\text{PM}_{2.5}$ $\text{concentration}_{std} = \text{Total PM}_{2.5}\ \text{Mass}/V_{std}$

$= 700\ \mu\text{g}/23.53\ \text{m}^3 = 29.75\ \mu\text{g/m}^3$ or $29.8\ \mu\text{g/m}^3$

Or correct the concentration for Standard Conditions:

$\text{PM}_{2.5}\ \text{concentration}_{std} = \text{PM}_{2.5}\ \text{concentration}_{act}\ (P_{std}/P_{act})(T_{act}/T_{std})$

$= 29.5\ \mu\text{g/m}^3 \times (760\ \text{mm Hg}/\ 740\ \text{mm Hg}) \times (293\ \text{K}/298\ \text{K})$

$= 29.79\ \mu\text{g/m}^3$ or $29.8\ \mu\text{g/m}^3$

Problem 2: PM2.5 Sampling
A $\text{PM}_{2.5}$ filter weighed 143.300 mg before sampling and 143.700 mg after sampling. The flow rate at atmospheric conditions of 745 mm Hg and 23° C was 16.7 L/min. The sampling period was 24 hours. What is the $\text{PM}_{2.5}$ concentration in $\mu\text{g/m}^3$ at actual atmospheric conditions?

Solution:

Mass = Final weight - initial (tare) weight

Mass = 143.700 mg – 143.300 mg = 0.400 mg × 1,000 μg/mg = 400 μg

Sampling time (t) = 24.0 hrs × 60 min/hr = 1,440 min

$V_{act} = Q_{act} \times t$

$V_{act} = 16.7\ \text{L/min} \times 1{,}440\ \text{min} = 24{,}048\ \text{L} \times \text{m}^3/1{,}000\text{L} = 24.05\ \text{m}^3$

$\text{PM}_{2.5}\ \text{concentration}_{act} = \text{Total PM}_{2.5}\ \text{Mass}/V_{act}$

$\text{PM}_{2.5}\ \text{concentration}_{act} = 400\ \mu\text{g}/24.05\ \text{m}^3 = 16.63\ \mu\text{g/m}^3$ or $16.6\ \mu\text{g/m}^3$

5.6 FRM and FEM for the Determination of Coarse Particles (PM_{10}-$PM_{2.5}$)

Coarse particles consist of PM_{10} subtracted by $PM_{2.5}$ (PM_{10}-$PM_{2.5}$). Several sites, mostly SLAMS sites in the National Core (NCore) network, require the measurement of coarse particles. Additionally, the characterization of coarse particles is important in case a PM_{10}-$PM_{2.5}$ mass concentration standard is developed in the future.

Coarse particles are sampled by FRM and/or FEM methods. Three classes of FEMs exist, ranging from methods with minor deviations from the FRM as Class I, to continuous methods as Class III. Instruments such as the dichotomous sampler are considered as Class II. FRM and FEM Class I samplers consist of two collocated samplers, where one sampler is operated with a PM_{10} size selector while the other is operated with a $PM_{2.5}$ size selector (i.e. WINS impactor or Very Sharp Cut Cyclone). FRM and FEM designations are discussed below.

For FRM determination of PM_{10}-$PM_{2.5}$, the $PM_{2.5}$ sampler of the $PM_{10-2.5}$ sampler pair must be verified to be either currently designated under 40 CFR Part 53 as a FRM for $PM_{2.5}$, or be shown to meet all requirements for designation as a FRM for $PM_{2.5}$, in accordance with requirements in 40 CFR Part 53. The PM_{10} sampler of the $PM_{10-2.5}$ sampler pair must be verified to be of like manufacturer, design, configuration, and fabrication to the $PM_{2.5}$ sampler of the $PM_{10-2.5}$ sampler pair, except for replacement of the particle size separator specified in Appendix L to CFR Part 50 with the downtube extension as specified in Figure O–1 of Appendix O, CFR Part 50. Essentially, sampling for the FRM method for PM_{10}-$PM_{2.5}$ consists of two identical FRM samplers, collocated and run concurrently, with one measuring PM_{10} and the other $PM_{2.5}$.

For FEM Class I determination of PM_{10}-$PM_{2.5}$, the $PM_{2.5}$ sampler of the $PM_{10-2.5}$ sampler pair shall be verified to be either currently designated in 40 CFR Part 53 as a FRM or Class I FEM for $PM_{2.5}$, or be shown to meet all requirements for designation as a FRM or Class I FEM for $PM_{2.5}$, in accordance with 40 CFR Part 53. The PM_{10} sampler of the $PM_{10-2.5}$ sampler pair must be verified to be of similar design to the $PM_{10-2.5}$ sampler and meet all requirements for designation as a FRM or Class I FRM for $PM_{2.5}$, as outlined in 40 CFR Part 53, except for replacement of the particle size separator specified in Appendix L of 40 CFR Part 50 with the downtube extension as specified in Figure O–1 of Appendix O of 40 CFR Part 50. In both the FRM and FEM Class I configurations, mass concentration from the PM_{10} sampler is subtracted by that of the $PM_{2.5}$ sampler in order to determine the coarse particle (PM_{10}-$PM_{2.5}$) mass concentration.

FEM Class II (i.e. dichotomous) and Class III (automated, continuous methods) requirements are currently being developed by EPA by collocating candidate Class II and Class III samplers with FRMs at several locations across the country. Class III analyzers must be capable of providing ambient air measurements representative of one-hour or less integrated $PM_{2.5}$ or $PM_{10\text{-}2.5}$

concentrations as well as 24-hour measurements determined as, or equivalent to, the mean of 24 one-hour consecutive measurements.

5.7 $PM_{2.5}$ Speciation Sampling

The EPA's Speciation Trends Network (STN), State and Local Air Monitoring Stations Network (SLAMS), and the National Parks Service's Interagency Monitoring of Protected Visual Environments (IMPROVE) network provide speciated $PM_{2.5}$ measurements for approximately 200 urban and 170 rural locations across the United States. The purpose of speciation sampling is to better understand the chemical composition of $PM_{2.5,}$ since the "single channel" Federal Reference Method is not capable of completely supporting a comprehensive set of analyses required to characterize the components of a $PM_{2.5}$ sample. Results from speciation sampling show that sulfate, nitrate, and organic carbon are the major components of $PM_{2.5}$ in ambient air.

The $PM_{2.5}$ target analytes in STN/SLAMS are similar to those within the Interagency Monitoring of Protected Visual Environments (IMPROVE) program and consist of an array of cations, anions, carbon species, and trace elements. Each series of analytes requires sample collection on the appropriate filter medium to allow chemical analysis with methods of adequate sensitivity. The methods used for analyses of these filter media include gravimetry (electro-microbalance) for total mass; energy dispersive X-ray fluorescence (EDXRF) for trace elements; ion chromatography (IC) for anions and cations; and controlled-combustion thermal optical reflectance (TOR) analysis for carbon.

The 40 CFR Part 53 requirements for designation of reference and equivalent methods for $PM_{2.5}$ do not require designations for speciation monitors. Rather, it was decided that the selection of sampling devices for the speciation network be based on performance-based criteria while allowing flexibility to employ more than one sampling technique, and to encourage further development of new sampling technologies. Consequently, several types of speciation samplers have been developed (Figures 5-24 to 5-27). The performance-based criteria are based on the following design considerations:

Particle Size Inlets

The inlet cut-point and separation profile must be comparable to the FRM and be capable of removing particles which exceed the aerodynamic particle diameter of fine particulate matter. Size selective inlets typically use a variety of means to remove particles larger than the specified aerodynamic size, and the size cutoff is based on sample flow rate. The IMPROVE, RAAS™, and SASS™ use a cyclone; the MASS uses a $PM_{2.5}$ FRM WINS assembly.

Denuder

Denuders are used immediately behind the size-selective inlet to remove gases that interfere with the aerosol measurements, or to quantify the concentrations of gases that are precursors to secondary aerosols. Denuders take advantage of the fact that gas molecules diffuse through air much more rapidly than small particles. In speciation samplers, denuders are part of the sampler design primarily for the collection of gaseous-nitrate on the nylon filter. Denuders have specific efficiencies and capacities depending on the design and coating materials used.

Filter Types

Each series of target species requires sample collection on the appropriate filter medium and chemical analysis by methods of adequate selectivity, sensitivity, and reliability. The filter substrates used to collect particulate matter are chosen for compatibility with the species collected and the particular chemical analyses. Filter media include polytetrafluoroethylene (PTFE, also known as Teflon®), quartz, and nylon. PTFE filters are employed to obtain atmospheric particulate matter samples for mass concentration determination and for subsequent measurement of a wide variety of trace elements. Pre-fired quartz fiber filters are used to collect samples for determination of atmospheric carbonaceous aerosol concentrations. The nylon filter is used to capture nitrate species and water-soluble anions and cations.

Flow Rate Measurement

Flow measurement and control for the speciation network are expected to be similar to the $PM_{2.5}$ FRM requirements. The sampling system shall have a sample air flow rate control capable of providing a sample air volumetric flow rate, measured over intervals of not more than 5 minutes over a 24-hour period, which should not vary more than ± 5 percent from the manufacturer's specified flow rate over the entire sampling period. Having tight control of sampler flow rate is a critical component of the speciation program, since calculations of ambient air concentrations require knowing the volumetric flow rate through the sampler.

Filter Temperature Measurement

Filter temperature measurement and control is an important element of the $PM_{2.5}$ chemical speciation network. This is due to the characteristics of the aerosols that are being captured. If sampler performance resulted in significantly higher temperature at the sample media compared to the ambient temperature, then volatile chemical species may be underestimated. If filter media were colder than ambient temperature, as may be the case during a rapid temperature rise in the morning under conditions of a very low dew point, then more volatile chemical species may be trapped in the sample media than otherwise would occur under normal conditions. Consequently, it is necessary for the sampler to provide a means to limit the temperature fluctuations and to monitor both ambient and filter media temperatures. The temperature should not differ from the transfer or independent temperature standard by more than ±2 °C.

Barometric Pressure Measurement

The sampler must have the capability to measure barometric pressure and record the maximum, minimum, and mean measurements over the sampling period. The barometric pressure measurement is used for the purpose of computing the actual sample collection volume. The pressure should not differ from the transfer or independent pressure standard by more than ±10 mm Hg.

Relative Humidity Measurement
When relative humidity is above 70%, particle growth due to accumulation may become significant. The capability for the sampler to measure ambient relative humidity is useful for input into the overall data interpretation process.

Physical and chemical speciation data are used to provide information on:

- assessing trends in mass component concentrations and related emissions, including specific source categories,
- characterizing annual and seasonal spatial variation of aerosols,
- determining the effectiveness of implementation control strategies,
- helping to implement the $PM_{2.5}$ standard by using speciated data as input to air quality modeling analyses,
- aiding the interpretation of health studies by linking effects to $PM_{2.5}$ constituents, and
- understanding the effects of atmospheric constituents on visibility impairment and regional haze.

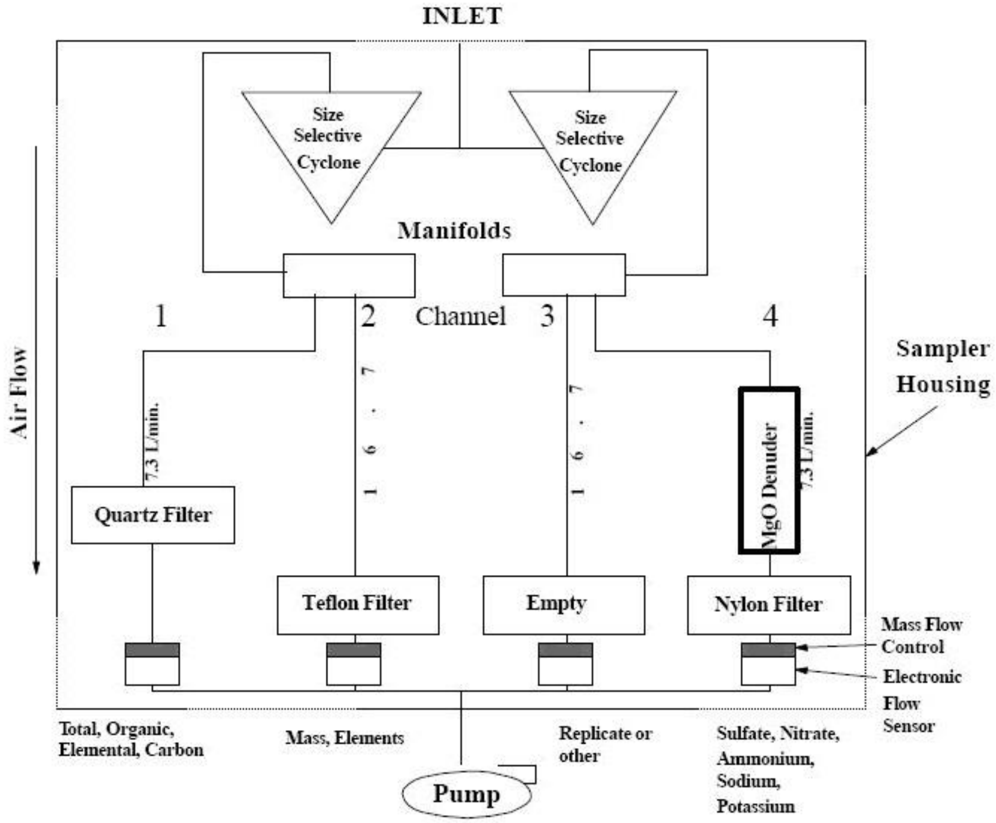


Figure 5-24. Schematic diagram of the Andersen Reference Ambient Air Sampler (RAAS™).

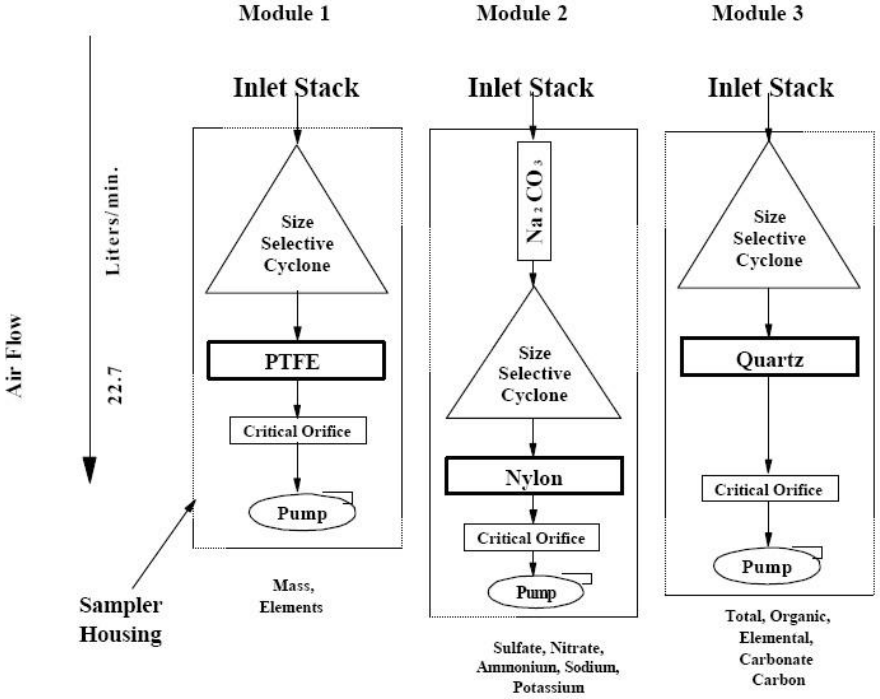


Figure 5-25. Schematic diagram of the IMPROVE sampler modules.

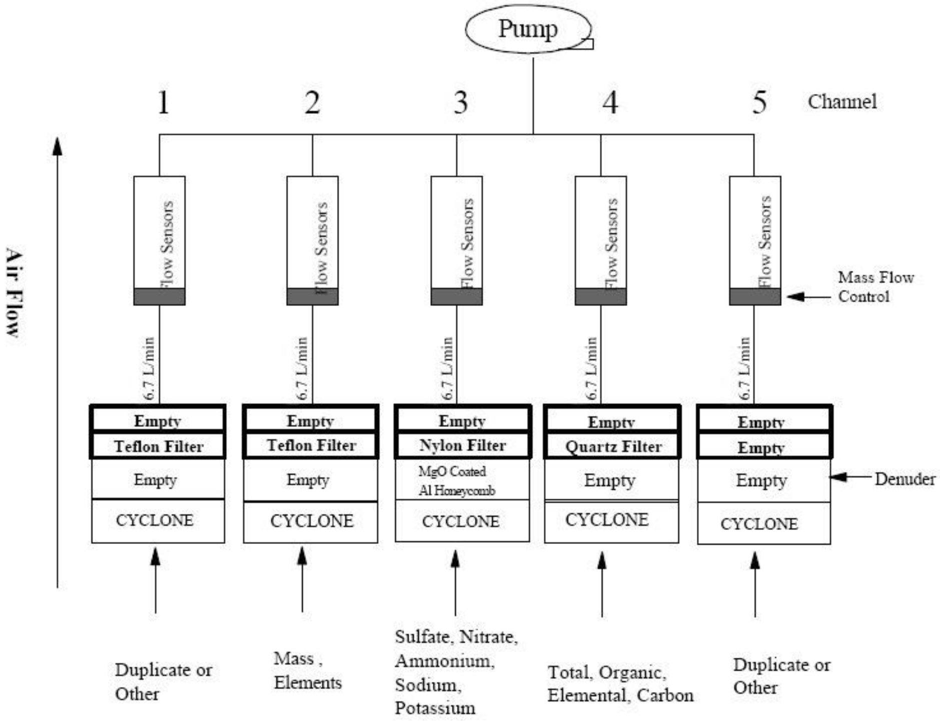


Figure 5-26. Schematic diagram of the MET ONE SASS™ sampling system.

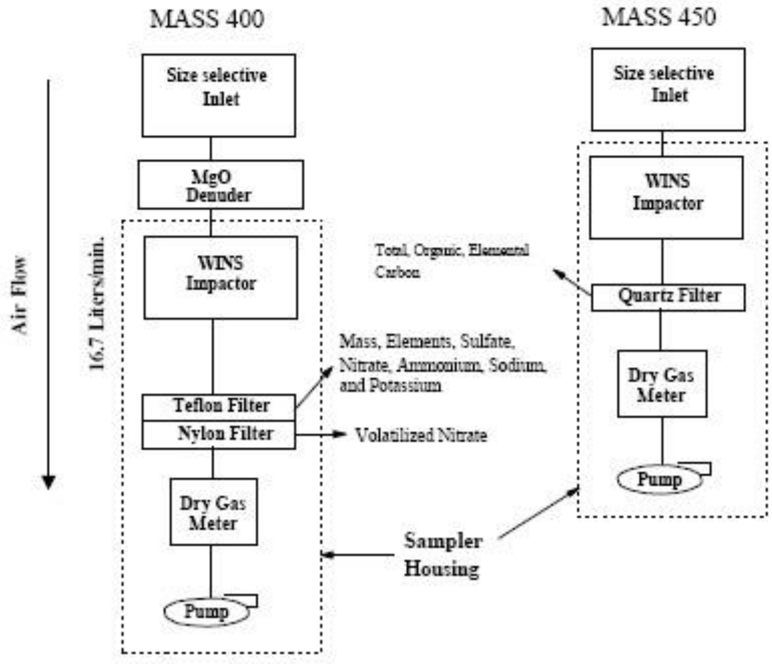


Figure 5-27. Schematic diagram of the URG Mass Aerosol Speciation Sampler (MASS).

5.8 Continuous *in situ* Monitoring for Particulate Matter

Continuous *in situ* particulate matter (PM) monitors measure at least one characteristic or property of aerosols (particles suspended in air) for quantification and/or characterization purposes. Continuous, automated monitors have been used to obtain PM mass concentration, particle size distribution, and chemical speciation information. Continuous monitors can be approved by EPA as a Class III Federal Equivalent Method (FEM) or Approved Regional Methods (ARMs).

Although not deemed Federal Reference Methods, several continuous mass concentration instruments have met requirements for federal equivalence status. The main advantage of continuous instruments is their ability to provide time-resolved measurements, which is not possible in filter-based methods. Continuous monitors are intended to:

- provide improved temporal resolution to better understand the sources and causes of elevated $PM_{2.5}$ concentrations in the atmosphere,
- facilitate public reporting of $PM_{2.5}$ air quality,
- reduce site visits and network operation costs, and
- implement periodic control strategies.

Continuous PM measurements have a large role in NCore (National Core) and SLAMS (State and Local Air Monitoring Stations) air quality networks. Although the SLAMS network includes NCore, PAMS, and all other state or locally operated stations not designated as special purpose monitor (SPM) stations, not all SLAMS sites are NCore sites. For this reason, requirements for continuous monitoring instruments are discussed separately for NCore and SLAMS below.

National Core (NCore)

There is at least one NCore site in each state, and each NCore site, at a minimum, must be able to provide the following PM information: 1) $PM_{2.5}$ particle mass using continuous and integrated/filter-based samplers, 2) speciated $PM_{2.5}$, 3) $PM_{10–2.5}$ particle mass, and 4) speciated $PM_{10–2.5}$. Several sites are capable of continuous $PM_{10-2.5}$ mass concentration. These sites are expected to complement the $PM_{2.5}$ data collection that takes place at non-NCore/SLAMS sites, and both types of sites can be used to meet the minimum $PM_{2.5}$ network requirements of NCore and/or SLAMS. Details on NCore can be found in 40 CFR Part 58 Appendix D and http://www.epa.gov/ttn/amtic/ncore/index.html.

State and Local Air Monitoring Stations (SLAMS)

$PM_{10-2.5}$ measurements are only required at SLAMS sites that additionally serve as NCore sites ($PM_{10-2.5}$ is required at NCore sites). Consequently, SLAMS-only sites do not require continuous PM_{10} measurements, although continuous $PM_{2.5}$ measurements are required. The minimum number of continuous $PM_{2.5}$ monitors at SLAMS sites depends on the site's Metropolitan Statistical Area classification (40 CFR Part 58 Appendix D, Table D-5). At least half of the $PM_{2.5}$ samplers at each site must be a continuously monitoring instrument. Additionally, at least one required continuous analyzer in each Metropolitan Statistical Area must be collocated with an FRM/FEM/ARM monitor, unless the continuous instrument has already been deemed a FEM or ARM monitor. In such cases, no collocation with an additional FRM, FEM, or ARM sampler is required. A current list of USEPA reference and equivalent methods can be found at http://www.epa.gov/ttn/amtic/criteria.html.

5.9 Automated Federal Equivalent Monitors

Instruments using two different measurement principles have received EPA's approval as equivalent methods (FEM) for PM_{10}. The first uses beta-radiation; the second uses an oscillating pendulum. Although these instruments can provide high-quality, time-resolved $PM_{2.5}$ data, automated equivalent methods have only recently been approved for $PM_{2.5}$. These two measurement principles, now featured by several vendors, are briefly discussed below.

Beta Attenuation Monitor (BAM)

The beta attenuation monitor samples at ambient conditions of temperature, relative humidity, and gas concentration to minimize particle volatilization biases. These monitors operate at a manufacturer-specified flow rate using an inlet hat, impactor, or cyclone to determine the 50% cut-point for the desired particle size to be measured. For beta attenuation monitors, low-energy, electron-emitting beta rays from a radioactive source are focused on sample deposits on a filter tape and detected on the opposite side. The beta intensity is described, to a good approximation, by the Beer-Lambert relationship. Common radioactive beta sources are Carbon-14 (C-14) and Krypton-85 (Kr-85), although Carbon-14 is more commonly used.

A continuous filter, commonly composed of glass fiber, is used in beta attenuation monitors. Typically, the attenuation through an unexposed portion of the filter tape is measured, and the tape is then exposed to the ambient sample flow where a deposit is accumulated. The beta attenuation is repeated, and the difference in attenuation between the blank filter and the deposit is a measure of the accumulated concentration.

A continuous measurement of aerosol mass concentration becomes possible when the beta attenuation coefficient per aerosol mass deposited on the filter is known. For example, the attenuation coefficient is $\sim 0.26\ \mathrm{cm^2/mg}$ for typical atmospheric aerosol using a Carbon 14 source. In continuous monitoring, movement of the filter tape is needed when the aerosol loading on the deposition spot attenuates the beta intensity at the detector to near background levels. Blank-corrected attenuation readings can be converted to mass concentrations for averaging times as short as 30 minutes. While these monitors are capable of producing half-hourly average mass concentrations, a 24-hour averaging period is required for typical ambient concentrations to obtain sufficient particulate deposition for accurate determination.

BAMs are typically operated at ambient temperatures and relative humidity. While these conditions preserve the integrity of volatile nitrates and organic compounds, they also favor the sampling of liquid water associated with soluble species at high humidities. Under these conditions BAM concentrations are often larger than those of collocated filter samplers for which samples have been equilibrated at lower laboratory relative humidities prior to gravimetric analysis. Sampled air can be preceded by a diffusion dryer to remove water vapor, thereby encouraging the evaporation of liquid water associated with soluble components of suspended particles.

A schematic of the beta attenuation measurement principle is shown in Figure 5-28:

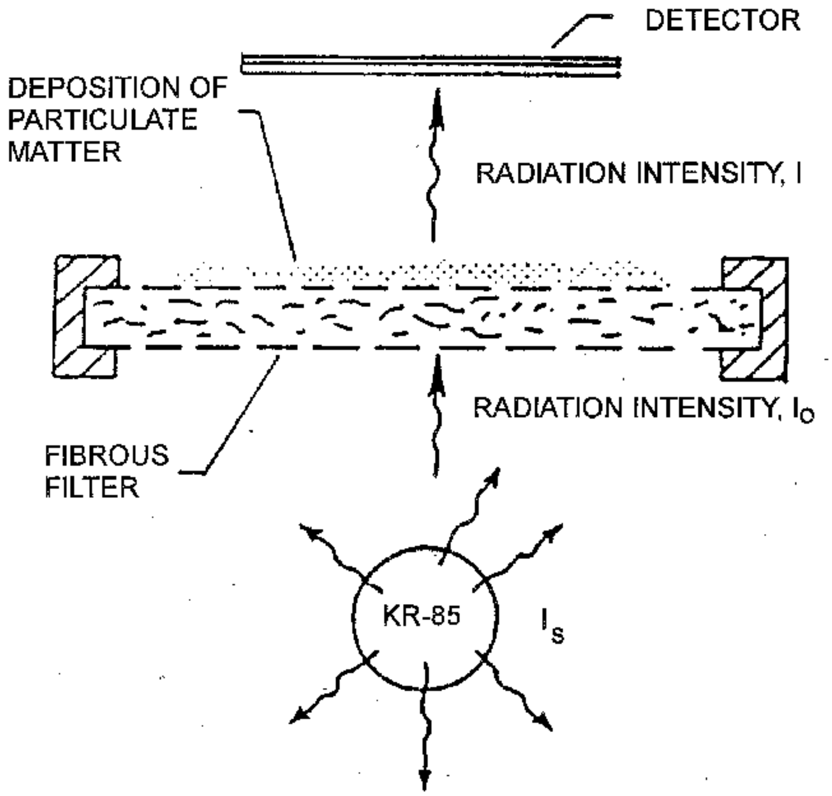


Figure 5-28. Measurement principle of beta attenuation analyzers.

Tapering Element Oscillating Microbalance (TEOM®)

The TEOM® primary operating mechanism is the microbalance system, which relies upon changes in the frequency of an oscillating tapered element to determine changes in the particulate mass collected. Many state agencies obtain $PM_{2.5}$ and PM_{10} TEOM® mass concentration data, although only the PM_{10} configuration has been approved as a federal equivalent method. The TEOM® ambient particulate monitor can provide averaging times from 10 minutes to 24 hours, and has a measurement range between 5 $\mu g/m^3$ and several g/m^3.

In the TEOM®, particle-laden air is drawn into the TEOM® monitor through an air inlet (TSP, PM_{10}, $PM_{2.5}$, or $PM_{1.0}$ inlets are available), followed by an exchangeable filter cartridge, where the particulate mass collects (filter lifetimes are approximately 2-4 weeks). The typical flow rate used for the TEOM® is 3 liters per minute, although it can be operated at flow rates between 0.5 and 5 liters per minute. The filtered air then proceeds through the sensor unit, which consists of a patented microbalance system. The microbalance system is discussed in more detail in the next paragraph. As the sample stream moves into the microbalance system (filter cartridge and oscillating hollow tapered tube), it is heated to the temperature specified by the control unit. The temperature default is usually 50 °C to prevent the measurement of particle-bound water. This is done to minimize the deposition of water due to changes in ambient humidity. It should be noted, however, that a default temperature of 50 °C can volatilize most of the ammonium nitrate and some of the volatile organic compounds in atmospheric particles. Consequently, monitored sites and seasons having high levels of ammonium nitrate and/or organic particulate mass do not always yield a reasonable correspondence between time-integrated TEOM® and collocated filter measurements.

The TEOM® microbalance system is quite unique. The TEOM® draws air through a hollow tapered tube, with the wide end of the tube fixed, while the narrow end oscillates in response to an applied electric field. The narrow end of the tube carries the filter cartridge. The sampled air stream passes from the sampling inlet, through the filter and tube, to a flow controller. The tube-filter unit acts as a simple harmonic oscillator described by the following equation:

(Eq. 5-6)

$$\omega = \left(\frac{k}{m}\right)^{0.5}$$

Where: ω = *the angular frequency,*
k = *the restoring force constant, and*
m = *the oscillating mass*

As particles are collected on the filter, the oscillating mass changes and results in a change of the oscillating frequency. An electronic control system maintains the tapered tube in oscillation and continuously measures this oscillating frequency. Basically, changes in PM mass are correlated to changes of the TEOM® oscillating frequency. To calibrate the system, the restoring force constant (k) is determined by placing a gravimetrically determined calibration mass on the filter and recording the frequency change due to this mass.

Details regarding the operation, calibration, and maintenance of several EPA-approved continuous and filter-based instruments can be found at the following website: http://www.epa.gov/ttn/amtic/inorg.html.

5.10 Other Automated PM Methods

Several other automated methods have been developed and used by researchers and air pollution professionals in order to better characterize particulate matter. These methods, described below, have been used for a variety of purposes, including outdoor and indoor air monitoring, industrial hygiene, and personal exposure assessment. Although many of the following methods are not commonly used by federal, state, local, and tribal agencies, they can be quite useful in obtaining time-resolved or semi-continuous information on mass concentration, total number of particles in specific size ranges, and elemental composition of particulate matter. In fact, continuous instruments measuring mass concentration may receive future approval as Class III FEMs, and can possibly be used as ARMs by state, local, and tribal agencies.

All continuous monitoring methods not previously discussed are discussed below by measurement principle. Much of the information presented below is based on the following EPA document: *Guidance for Using Continuous Monitors in* $PM_{2.5}$ *Monitoring Networks* (March 3, 1998). This document can be found at the following URL: http://www.epa.gov/ttnamti1/files/ambient/pm25/r-98-012.pdf. Detailed information regarding each instrument can be found via sources cited within the text of the *Guidance* document.

Mass and Mass Equivalent

In mass and mass equivalent instruments, particle mass is determined by its inertia, electron attenuation properties, or by the decrease in pressure across small pores in a filter. In addition to the Beta Attenuation Monitor (BAM) and Tapering Element Oscillating Microbalance® (TEOM®) discussed in the previous section, two commonly used mass and mass equivalent instruments are discussed below.

Piezoelectric Microbalance

Piezoelectric crystals have mechanical resonances that can be excited by applying an alternating electrical voltage to the crystal. As the resonance frequencies are very well defined, such crystals (quartz in particular) have found applications as secondary time and frequency standards in clocks and watches. As for all mechanical resonators, the resonance frequency is a function of mass. Therefore, by monitoring the resonance frequency in comparison with a second crystal, one can continuously measure the mass deposited on the crystal. Comparison with a second crystal largely compensates for the effect of temperature changes on the resonance frequency.

The piezoelectric principle has been used to measure particle mass by depositing the particles on the crystal surface either by electrostatic precipitation or by impaction. The collection efficiency of either mechanism has to be determined as a function of particle size to achieve quantitative measurements. In addition, the mechanical coupling of large particles to the crystal is uncertain. Both single and multi-stage impactors have been used to collect particles by size range. Quartz crystals have sensitivities of several hundred hertz per microgram. This sensitivity results in the ability to measure the mass concentration of a typical 100 $\mu g/m^3$ aerosol to within a few percent in less than one minute.

Pressure Drop Tape Sampler (CAMMS)

A continuous particle mass monitoring system, CAMMS (continuous ambient mass monitor system), is based on measuring the pressure drop across a porous Fluoropore membrane filter. This pressure drop is linearly correlated to the particle mass deposited on the filter. The filter face velocity is chosen such that pore obstruction by interception is the dominant cause of particle-related pressure drop change over time. The monitor consists of: 1) a Fluoropore filter tape to collect particles; 2) a filter tape transportation system to allow for several weeks of unattended particle sampling; 3) a system to measure the pressure drop across the filter; 4) a diffusion dryer to remove particle-bound water; and 5) an air sampling pump. The monitor exposes a new segment of filter tape every 20 to

60 minutes for particle collection. During this period, particles collected on the filter should remain in equilibrium with the sample air, since the composition of ambient air does not usually vary substantially over this short time period. Volatilization and adsorption artifacts are minimized because measurements are made at ambient temperature for short time periods and at a low face velocity. A diffusion dryer that removes water vapor could also be used to condition air, thereby encouraging the evaporation of liquid water associated with soluble components of suspended particles. The CAMMS can detect concentrations as low as 2 $\mu g/m^3$ for hourly averaged measurements.

Visible Light Scattering

Particle light scattering (bsp) is determined by illuminating particles, individually or as a group, and measuring the scattered intensity at different orientations from the incident light source. The intensity of scattered light is related to mass concentration by electromagnetic theory or by comparison with a collocated filter measurement. Particle light scattering measurements from five different types of instruments are discussed in the following subsections.

Nephelometer

Nephelometers, as a whole, are highly versatile instruments that quantify particle light scattering. Integrating nephelometers quantify particle light scattering integrated over all directions. For visibility applications, scattering extinction serves as a surrogate for total light extinction which is related to visibility.

Other applications of the integrating nephelometer include: 1) measurements of Rayleigh scattering coefficients, 2) determination of aerosol size distributions and refractive indices, 3) detection of sulfuric acid - ammonium sulfate aerosol; and 4) estimation of particle mass concentrations.

Nephelometer sampling procedures depend on the intended uses of the data. To determine visibility reduction, total light scattering is desired, including light scattering caused by 1) liquid water associated with soluble particles and 2) molecules in clean air.

Mass concentration measurements from nephelometers are typically overestimated once relative humidity is above 80%. This is due to the fact that small particles grow to sizes that scatter light more efficiently as they acquire liquid water at approximately 80% relative humidity. To compensate for this, the air stream can be heated, similar to TEOM® air conditioning, to remove liquid water when an indicator of particle mass is desired. Some systems are able to control both temperature and humidity to characterize the hygroscopic properties of suspended particles. Such heating mechanisms, however, can increase the volatilization of ammonium nitrate and volatile organic compounds from particles. Although light scattering is often highly correlated with mass concentrations, this relationship depends on several variables and may be different from location to location and for different seasons of the year.

Particle scattering measured by integrating nephelometers includes systematic errors owing to: 1) non-monochromatic light sources; 2) limits of the integration angle; and 3) and non-Lambertian light sources. Further modification of the nephelometer response can also be achieved by adding a size-selective inlet to the nephelometer air intake.

Optical Particle Counter (OPC)

Optical Particle Counters (OPC) use light scattering to detect the size and number of individual particles. OPCs have long been used in aerosol research, thereby attaining a degree of reliability and ease of operation that allow them to be deployed in long-term monitoring networks. Some instruments analyze the spatial distribution of the scattered light to derive a shape parameter that can be used to determine deviations from sphericity.

In an OPC, a narrow air stream is directed through a small sensing zone, where it is illuminated by an intensive light beam, commonly a visible laser beam. Light scattered by an individual particle is sensed by a fast and sensitive detector, resulting in an electrical pulse. Particle size is determined from the pulse amplitude, and particle number is determined from the number of pulses. The size of particles that can be detected with OPCs ranges from about 0.05 to 50 μ, but it is more typically 0.2 to 30 μm.

Particle sizes and numbers are translated to mass concentration by assuming a spherical particle shape and a particle density. The sum over all particle size bins can be further related to mass loadings by comparison with a collocated filter sample. Some particle counters allow a 47-mm filter to be placed in the exhaust stream so that the sensed particles can be collected for laboratory weighing and possible chemical characterization.

A purge filter is typically used to pre-zero the OPC before each set of measurements is taken. Once a year, the OPC is typically sent to the manufacturer for calibration with a National Institute of Standards and Technology (NIST)-traceable, monodisperse distribution of polystyrene latex spheres. While size measurements with OPCs can be very precise, their accuracy depends on particle composition and shape. These issues have been explored for atmospheric aerosols. Accuracy can be improved by simultaneous use of an integrating nephelometer with optical particle counters.

Condensation Nuclei Counter (CNC)

Continuous-flow Condensation Nuclei Counters (CNC) sense ultrafine particles by causing them to grow to a size that is efficiently detected by light scattering. Particles in a sampled air stream enter a saturator where alcohol vapors at a temperature typically above ambient (e.g., 35 °C) create a saturated atmosphere. Particles then pass into a condenser tube at a temperature sufficiently below that of the saturator (e.g., 10 °C). Alcohol vapor condenses on the particles causing them to grow, and they are detected and classified by an OPC. CNCs detect particles with 0.003 to 1 μm diameters. For low particle concentrations, the instrument operates in a counting mode, registering individual light pulses. For concentrations above 1,000 particles/cm^3, the simultaneous presence of more than one particle in the viewing volume becomes frequent, and individual particles can no longer be counted. At this point, the CNC switches to the photometric mode where the power of the light scattered by all particles present in the viewing volume is measured. In the counting mode, a CNC can be very precise, but the counting efficiency for ultrafine particles depends substantially on the instrument design. In the photometric mode, the CNC must be calibrated with an aerosol of known concentration (for example, by using an electrostatic classifier). Response curves as a function of particle size, concentration, and different environmental conditions have been determined for several different CNCs.

CNCs are the most practical instruments for determining ultrafine particle concentrations, but they are not as accurate as other continuous methods for determining $PM_{2.5}$ or larger size fractions owing to the low upper limit of their size range.

Aerodynamic Particle Sizer (APS)

The Aerodynamic Particle Sizer (APS) measures light scattering as well as the time-of-flight of sampled particles. The measured aerodynamic diameter can be converted to volume-equivalent diameter or mobility-equivalent diameter. The APS accelerates the air stream in a converging nozzle. Particles have a larger inertia than the gaseous component, and therefore lag in acceleration and speed behind the air stream. Particles with higher mass (as a result of higher density or larger size) achieve lower velocities than those with lower mass. Each particle is detected by laser scattering at the beginning and end of a fixed path length to determine the time taken to traverse this path (the "time-of-flight"). The flight times are related to particle mass. The APS measures particles with diameters of 0.5 to 30 μm.

The APS aerodynamic diameter differs from the standard definition of aerodynamic diameter (the diameter of the unit density sphere that has the same settling velocity in still air). The APS aerodynamic diameter is adjusted for particle density, ambient gas density, and ambient air viscosity. During the acceleration process, calibration and ambient particles can deform in different ways (i.e., flatten) depending on their viscosity. Nonspherical particles behave differently from spherical particles, necessitating additional adjustments. Phantom particle counts may result from the time-of-flight laser detection system.

Light Detection and Ranging (LIDAR)

Light Detection and Ranging (LIDAR) measures light scattered in the direction of the light source ("backscattering") along a sight path. Aerosol LIDAR determines aerosol distributions while Differential Absorption LIDAR (DIAL) can measure concentrations of several gases.

Several types of LIDAR are currently in-use. Basic single-wavelength aerosol LIDAR yields a semi-quantitative measurement of the backscatter coefficient. High-spectral-resolution and Raman LIDAR provide quantitative backscatter coefficients; these systems are very complex and currently not commercially available. The connection between backscatter coefficient and PM concentration is indirect and depends on particle size distribution and refractive index of the aerosol particles, similar to nephelometers. Aerosol LIDAR are more suitable for determining the spatial distribution of aerosol concentrations and its temporal development, than for quantifying mass concentrations.

A basic aerosol LIDAR system consists of a transmitter and a receiver located next to each other. The transmitter, typically a pulsed laser, sends a short pulse of collimated light into the atmosphere. A small part of this light pulse is scattered back into the receiver by suspended particles and gas molecules. The absolute system calibration is generally unknown. The LIDAR equation is, therefore, under-determined and cannot be solved without additional assumptions or data.

DIAL measurements are made at two different wavelengths with substantially different absorption coefficients for the gas of interest. DIAL LIDAR is a useful tool for continuous measurements of aerosol precursor gases. The range-resolved gas concentration is calculated from the ratio of the LIDAR signals at the two wavelengths. The laser line wavelength with the larger absorption coefficient is referred to as "on-line." The laser line with the smaller absorption coefficient is referred to as "off-line."

DIAL has been used for the measurement of a number of relevant tropospheric trace gases including ozone (O_3), sulfur dioxide (SO_2), nitric oxide (NO), nitrogen dioxide (NO_2), ammonia, and aromatic hydrocarbons. Though commercially available, LIDAR systems are expensive and must be individually designed or modified for each specific application.

Visible Light Absorption

Black carbon (BC) (sometimes termed "elemental carbon," "light-absorbing carbon," or "soot") is the dominant visible light-absorbing particulate species in the troposphere and mostly results from anthropogenic combustion sources. It is usually found in the nucleation or accumulation mode for particles well under 1 µm in equivalent dimensions (i.e., if chain aggregates were consolidated into a single sphere). Mass loadings range from a few ng/m^3 in remote pristine regions or over oceans distant from land, to a fraction of 1 µg/m^3 in rural regions of the continents, and exceed 1 µg/m^3 in many cities.

Continuous methods that monitor particle light absorption (b_{ap}) can also be used to measure the $PM_{2.5}$ component consisting of light-absorbing particles. Attenuation of light through a filter and photoacoustic oscillation are detection principles used to quantify particle absorption as a surrogate for black carbon. Particle light absorption measurements from three different instruments are discussed in the following subsections.

Aethalometer and Particle Soot/Absorption Photometers

Light-absorbing aerosol (e.g., BC) deposited on a filter can be quantified through the measurement of light transmission or reflection. For example, initial methods, such as the British Smoke method in the early 1950s, were first used to visually characterize the reflectance of a filter sample. In their more advanced configurations, a clean portion of a filter tape was periodically moved into the sampling position, thereby allowing diurnal variations (typically hourly averages) in particle concentrations to be recorded. In these methods, the optical density of the particle deposit is determined from the logarithm of the ratio of intensities measured on the filter with and without the deposit.

A more quantitative method, the integrating sphere method, measures aerosol light absorption by placing the loaded filter in an integrating sphere and illuminating it. Light, both transmitted and scattered by the loaded filter, first reaches the diffusely reflecting surface of the sphere where it is homogenized, and then the light is detected by the photodetector. The difference between a clean filter and one loaded with particles gives the amount of light absorbed by the particles. Simplifications of the integrating sphere method, such as the integrating plate or sandwich methods, are most often used for routine measurements.

A real-time version of the integrating plate method, the aethalometer, continuously collects aerosol on a quartz-fiber filter tape. During the deposition process, the light attenuation through the aerosol collection spot and an unloaded reference spot are monitored. Their difference yields the absorption due to the integral of all light-absorbing materials collected on a particular spot. The time derivative of this quantity is a measure of the current aerosol light absorption. When the optical density of the aerosol spot reaches a certain value, the filter tape advances automatically. Time resolution available with the aethalometer varies from seconds or minutes in urban areas to ten minutes in rural locations and longer in very remote locations. One filter tape is sufficient for approximately 700 aerosol collection spots corresponding to one or more months of operation in urban areas, or a year or more in rural areas.

The aethalometer converts the result of its filter attenuation measurement into BC mass concentration by a conversion factor of 19.2 m^2/g. Aethalometer BC generally agrees well with collocated filter samples analyzed for elemental carbon by thermal optical methods. Applications of the aethalometer include air quality monitoring in urban and more remote locations, transport studies, and source characterization.

The Particle Soot/Absorption Photometer (PSAP) gives a filter-based, real-time measurement of aerosol light absorption. The PSAP produces a continuous measurement of absorption by monitoring the change in transmittance across a filter for two areas on the filter, a particle deposition area and a reference area. A light emitting diode (LED) operating at 550 nm, followed by an Opal glass, serves as light source. The absorption reported by the PSAP is calculated with a nonlinear equation correcting for the magnification of absorption by the filter medium and for response nonlinearities as the filter is loaded. Measurement time resolution can be as short as a few seconds to five minutes, depending on ambient aerosol light absorption. Applications of the PSAP include its use in ground-based monitoring by NOAA's Climate Monitoring and Diagnostics Laboratory (CMDL) and in field campaigns such as the Aerosol Characterization Experiment (ACE) of the International Global Atmospheric Chemistry (IGAC) program.

Photoacoustic Spectroscopy

At atmospheric pressures, electromagnetic energy absorbed by particles changes to thermal energy, thereby heating the particles and the surrounding gases. Increased gas temperatures surrounding light-absorbing particles cause thermal expansion of the gas. When the light source power is modulated, the periodic expansion of the gas results in a sound wave at the modulation frequency, which may be detected with a microphone. This "photoacoustic" detection of particle light absorption can be related to the black carbon concentration.

Sensitive photoacoustic techniques use a power-modulated laser as light source. By placing the aerosol-laden air into an acoustic resonator, and modulating the laser power at its resonance frequency, the varying pressure disturbance (acoustic signal) is amplified by the buildup of a standing acoustic wave in the resonator.

Electrical Mobility

Electrical mobility analyzers are applicable to particles smaller than 1 µm. They are the only practical alternative to the Condensation Nuclei Counter (CNC) instrument for quantifying the ultrafine fraction of the particle size distribution. The resulting particle size is known as mobility equivalent diameter, which can be converted to volume equivalent diameter or aerodynamic diameter.

A basic electrical mobility analyzer consists of: 1) a charger to impart an electric charge to the particles (a diffusion charger that exposes particles to unipolar positive ions is commonly used); 2) a classifier that separates the particles by acting on their electrical charge and mass; and 3) a detector to monitor the separated particles.

Electrical mobility analyzers are often used together with aerodynamic particle sizers, with the electrical mobility analyzer capturing particles below 1 µm and the aerodynamic particle sizers measuring the larger particles. Particle number measurements with two different instruments are discussed in the following subsections.

Electrical Aerosol Analyzer (EAA)

The Electrical Aerosol Analyzer (EAA) has been widely applied and characterized in aerosol studies. EAAs are typically operated with about ten size channels covering the range from 0.01 to 1.0 µm with a measurement time on the order of a few minutes.

A positively charged aerosol enters a mobility tube consisting of two coaxial cylinders. The outer tube is grounded and a negative potential is applied to the inner tube. As the aerosol flows down the mobility tube, its mobile fraction is precipitated on the inner tube by electrical forces. The remaining aerosol is detected, commonly by an electrometer that measures the electrical current of the remaining aerosol. The potential (voltage) of the inner cylinder is changed in steps. For each potential, a different fraction of the aerosol is precipitated. The resulting current-versus-voltage curve for an aerosol can be converted into a current-versus-size curve once the EAA has been calibrated with monodisperse aerosol of known size. Calibration of the current sensitivity is done by grounding the inner cylinder and measuring the aerosol current without precipitation losses.

Differential Mobility Particle Sizer (DMPS)

The Differential Mobility Particle Sizer (DMPS) improves on the EAA by making measurements with much greater size resolution (e.g., 100 channels).

The DMPS is essentially a modification of the EAA. The basic difference is that the DMPS produces a flow of aerosol consisting of particles with an electrical mobility between two closely spaced values (i.e., differential), while the EAA produces a flow consisting of particles with an electrical mobility above some value (i.e., integral). Instead of measuring the flow of particles missing the inner tube as in the EAA, a sample flow of aerosol is extracted through a slot in the inner tube. Only particles with mobilities within a limited range enter the sample stream for detection. As in the EAA, the voltage of the inner tube is stepped through a number of values and the DMPS directly yields the electrical mobility distribution without further differentiation.

Measurement times for DMPS with electrometers as detectors can be on the order of one hour. Operation with a CNC as a detector can reduce the measurement time by an order of magnitude. A further order of magnitude reduction in averaging time can be achieved by scanning the inner tube voltage. This modification is referred to as a Scanning Mobility Particle Analyzer (SMPA).

The conventional DMPS utilizing a cylindrical geometry is limited for ultrafine particles (< 0.020 µm) as its transmission efficiency drops dramatically below 0.02 µm due to diffusion losses. The accessible size range can be extended down to 0.001 µm by either modifying the cylindrical DMPS or by changing to a radial geometry.

Chemical Components

If the carbonaceous, nitrate, sulfate, ammonium, and geological components of suspended particles could be determined continuously and *in situ*, a reliable speciated estimate of $PM_{2.5}$ or PM_{10} mass concentration could be derived. While most of these chemical-specific particle monitors are currently experimental, rapid technology advances will make them more available and more widely used within coming years. The following subsections introduce various versions of single particle mass spectrometers that measure particle size and chemical composition, along with single compound instruments to measure carbon, sulfur, and nitrate.

Single Particle Mass Spectrometers

Continuous versions of the Laser Microprobe Mass Spectrometer (LAMMS) have been developed as the Rapid Single particle Mass Spectrometer (RSMS), Particle Analysis by Laser Mass Spectrometry (PALMS), and Aerosol Time Of Flight Mass Spectrometry (ATOFMS). These devices measure the size and chemical composition of individual particles. More recently, instruments have been developed for ground-based monitoring and monitoring in the troposphere and lower stratosphere.

In SPMS analyzers, particles are introduced into a vacuum by a nozzle. The presence of particles is detected through light scattered from a visible laser beam. This scattering process is also used as an Optical Particle Counter (OPC) or Aerodynamic Particle Sizer (APS) to determine the size and number of particles passing through the instrument. The presence of a particle triggers a high-energy pulsed laser which, with a single pulse, vaporizes particle material and ionizes part of it. The ions are detected and analyzed by a time-of-flight mass spectrometer. The time particles spend in the vacuum is on the order of microseconds, minimizing condensation, evaporation, and reactions.

The analysis rate is limited by the repetition rate of the pulsed laser. The presence of the OPC makes it possible to analyze a size-selected fraction of the particles; however, it also imposes a lower limit on the particle size being analyzed, as very small particles are not detected by the OPC. Running a pulsed laser without triggering can acquire smaller particles, but at the expense of a lower duty cycle and no size selection. Because of the complicated ionization process, the technique is currently used more commonly to survey the chemical composition of particles than to yield quantitative mass concentrations of particle components.

Applications of this technique have included characterizing aerosol composition, examining the purity of laboratory-generated sulfuric acid droplets, determining halogens, speciating sulfur, studying matrix-assisted laser desorption/ionization, monitoring pyrotechnically-derived aerosol in the troposphere, characterizing automotive emissions, measuring marine aerosols and their radiative properties, and observing heterogeneous chemistry.

Carbon Analyzer

Various analyzers have been developed to determine ambient organic carbon (OC) and elemental carbon (EC). As previously mentioned, elemental carbon (EC), also known as black carbon (BC), can be measured by aethalometers. A recently available device, the multi-angle absorption photometer, has been designed to carry out continuous emission measurements of EC. This instrument measures atmospheric loading using a radiative transfer scheme to particle-loaded glass fiber filters. The EC content of collected particles on the filter tape is continuously determined at several angles by simultaneously measuring optical absorption and scattering of light. Detection limits for the multi-angle absorption photometer are as low as 100 ng/m^3 for a 2-minute sample and 20 ng/m^3 for a 30-minute sample. Various inlets (TSP, PM_{10}, $PM_{2.5}$, $PM_{1.0}$) are available for the multi-angle absorption photometer and other carbon analyzers.

A thermal method has been used in the past to determine hourly-averaged, continuous particulate OC and EC concentrations. Specifically, the Ambient Carbon Monitor Series 5400 by Rupprecht and Patashnick, Co., now discontinued, differentiated between OC and EC by dividing the measured amount of carbon released from an intermediate burn (default 250 °C) and a final burn (default 750°C), respectively, by the air volume that passed through the instrument during sample collection. Volatilized carbon in this instrument was detected by a NDIR CO_2 sensor. These instruments provide hourly, continuous measurements by collecting particles on one impaction collector (collection mode) while the other impaction collector is in analysis mode.

Thermal/optical methods have been typically used for semi-continuous measurements of both OC and EC. These instruments are considered semi-continuous since sample collection and the internal analysis of the collected sample cannot simultaneously occur. Typically, all carbon in the sample is converted to methane (CH_4) for quantification by a Flame Ionization Detector (FID). For a 30-minute sample, the minimum quantifiable levels are 0.5 $\mu g/m^3$ for OC and EC, respectively.

Sulfur Analyzer

Continuous methods for the quantification of particulate sulfur compounds first remove gaseous sulfur (e.g., SO_2, H_2S) from the sample stream by a diffusion tube denuder, followed by the analysis of particulate sulfur. Another approach is to measure total sulfur and gaseous sulfur separately by alternately removing particles from the sample stream, and aerosol sulfur is obtained as the difference between the total and gaseous sulfur. The total sulfur content is measured by a flame photometric detector (FPD) by introducing the sampling stream into a fuel-rich hydrogen-air flame that reduces sulfur compounds and measures the intensity of the S_2* chemiluminescence.

Because the formation of S_2* requires two sulfur atoms, the intensity of the chemiluminescence is theoretically proportional to the square of the concentration of molecules that contain a single sulfur atom. In practice, the relationship is between linear and square and depends on the sulfur compound being analyzed. Calibrations are performed using both particles and gases as standards. The FPD can also be replaced by a chemiluminescent reaction with ozone that minimizes the potential for interference with a faster time response.

Capabilities added to the basic system include *in situ* thermal analysis and sulfuric acid (H_2SO_4) speciation. Sensitivities for sulfur aerosols as low as 0.1 $\mu g/m^3$ with time resolution ranging from 1 to 30 minutes have been reported. Continuous measurements of aerosol sulfur content have also been obtained by on-line x-ray fluorescence analysis with a time resolution of 30 minutes or less.

Nitrate Analyzer

The Automated Particle Nitrate Monitor (APNM) provides a high-time-resolution measurement of particle nitrate concentration. It uses an integrated collection and vaporization cell whereby particles are collected by a humidified impaction process, and analyzed in place by flash vaporization in a nitrogen carrier gas. In the vaporization process, the evolved gases from particulate origin are quantified by a chemiluminescent analyzer operated in the NO_x mode. Time resolution of the instrument is on the order of 12 minutes, corresponding to a ten-minute collection followed by an analysis step of less than two minutes.

The humidifier plus flash vaporization approach is, in fact, similar to some manual methods for measuring the size distribution of sulfate aerosols. The difference, however, is that the particle collection and analysis has been combined into a single cell, thus allowing the system to be automated. Although the APNM method is specific to nitrate, the same technology could be applied for continuous sulfate measurements by using a sulfur detector instead of a nitric oxide detector.

Multi-Elemental Analyzer

Both streaker (PIXE International, Tallahassee, FL) and DRUM (Davis Rotating-drum Universal-size-cut Monitoring impactor) (University of California, Davis, CA) samplers provide continuous particle collection on filter substrates followed by laboratory elemental analysis with Particle-Induced X-Ray Emission (PIXE). This is a continuous but not an *in situ* real-time monitoring method, due to the lag time between sample collection and chemical analysis in a laboratory. These samplers have a time resolution of approximately one hour, and can supply high-time-resolution elemental concentrations.

Streaker

Ambient particles in the streaker sampler are collected on two impaction stages and an after-filter. The first impaction stage has a 10-µm cutpoint and collects particles on an oiled frit that does not move. The particles collected on this stage are discarded. The second impaction stage has a 2.5-µm cutpoint and collects coarse particles (PM_{10} minus $PM_{2.5}$) on a rotating Kapton substrate that is coated with Vaseline to minimize particle bounce. The second impaction stage is followed by a 0.4-µm-pore-size Nuclepore polycarbonate-membrane filter that has an 8-mm-long negative pressure orifice behind it to collect fine particles (nominally $PM_{2.5}$). The air flow rate through the streaker sampler is primarily controlled by the porosity of the filter and the area of the negative pressure orifice. A 1-mm-wide orifice can be set up to result in a flow rate of approximately 1 liter per minute and produce an annular deposit of 8 mm in width, with any point on the deposit collected during a one-hour time period.

The body of the streaker sampler has a cylindrical form with a diameter of approximately 10 cm and a length of about 20 cm. It contains a clock motor that advances two particle collection substrates mounted within the streaker. The streaker is mounted in the open air with the sample air inlet at the bottom to keep out very large particles (e.g., rain and drizzle). Sample air flow rates can be verified by a flow meter, temporarily attached to the inlet of the streaker sampler at the beginning and end of sampling on each substrate, or at times in between. Substrates of 168 mm in length have the capacity to accommodate a seven-day sampling period.

DRUM

The Davis Rotating-drum Universal-size-cut Monitoring Impactor (DRUM) is an eight-stage cascade impactor. It collects particles on grease-coated mylar substrates that cover the outside circular surface of eight clock-driven slowly rotating cylinders or drums (one for each stage). The advantages of the DRUM sampler are its capability to operate for up to thirty days unattended and its use of the location of particle deposits along the drum substrate as a means to determine the time of their collection. The DRUM collects aerosol from 0.07 µm to 15 µm in diameter for eight size ranges (0.07 to 0.24, 0.24 to 0.34, 0.34 to 0.56, 0.56 to 1.15, 1.15 to 2.5, 2.5 to 5.5, 5.5 to 10, and 10 to 15 µm), followed by focused-beam PIXE analysis. DRUM samplers have been used in several visibility field studies to confirm assumptions about mass scattering efficiency dependence on sulfur size distributions (e.g., Pitchford and Green, 1997).

The DRUM sampler, and other Lundgren-type rotating drum impactors, are unique among size-segregating samplers in that they generate a continuous time history of aerosol component size distributions with short time resolution (e.g., hourly). Unlike the conventional aerosol size distribution data sets with at most a few dozen distributions that can be individually scrutinized, the DRUM produces hundreds of distributions. In addition, time series analysis, summary statistics, and multivariate analysis can be applied to concentrations measured on any or all stages of the DRUM sampler.

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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_2CO_3) and ammonium hydroxide (NH_4OH). The solubilities of these acids and bases are much greater than gaseous CO_2 or NH_3. 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_2 and aqueous H_2O_2 to produce sulfuric acid. The concentration of SO_2 is determined by titrating the H_2SO_4 formed with Ba $(ClO_4)_2$. This procedure is currently the reference method for determining SO_2 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[1] 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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[1] 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 (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.

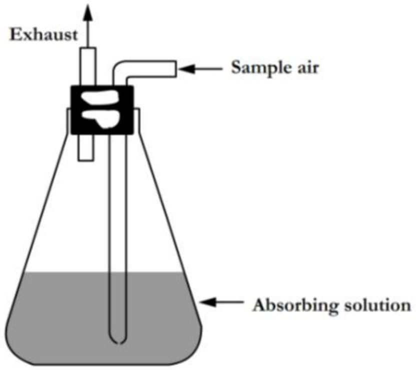

Figure 6-1. Absorption device adapted from an Erlenmeyer flash.

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.

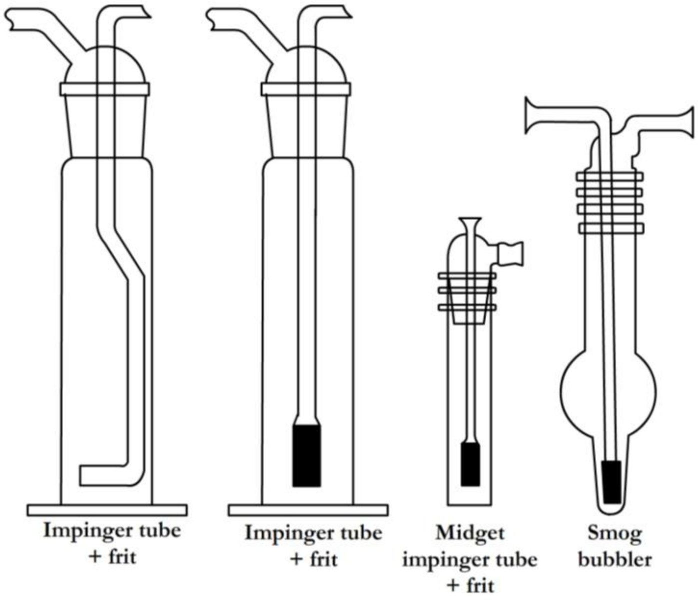

Figure 6-2. Typical fritted-glass absorbers.

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.

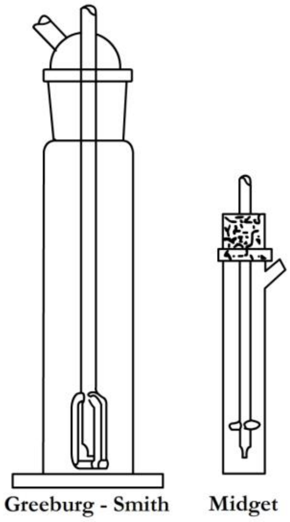

Figure 6-3. Two types of impingers.

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 midget 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 ±15-20% 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 absorbent 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[2] 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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[2] 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.

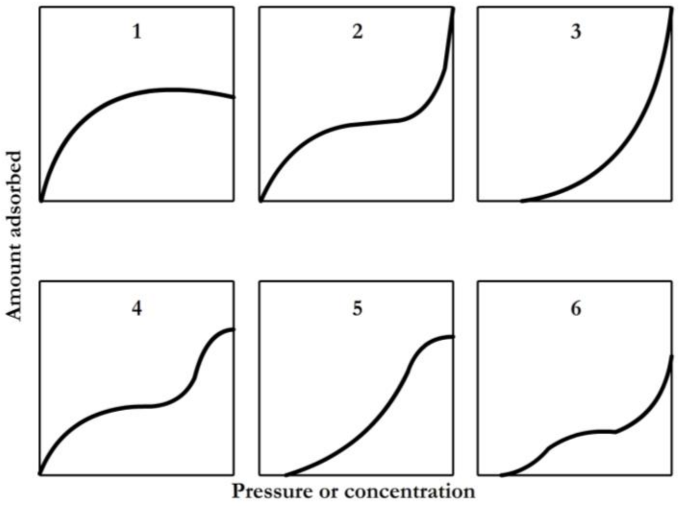

Figure 6-4. Gas adsorption isotherms.

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_2	4.7	33
N_2	8.0	126
CO	9.3	134
CH_4	16.2	190
CO_2	48.0	304
HCl	72.0	324
H_2S	99.0	373
NH_3	181.0	406
Cl_2	235.0	417
SO_2	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 absorbate 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^2/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 [$\dot{\mathrm{A}}$] = 1 x 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 $\dot{\mathrm{A}}$ in diameter, while methylene blue is excluded by pores having a diameter less than about 15 $\dot{\mathrm{A}}$.

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

Molecular Sieve

Molecular sieve adsorbents[3] are synthetic sodium or calcium alumino-silicate zeolites of very high porosity. They are another representative of the siliceous adsorbents.

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[3] Often referred to as molecular sieve absorbents.

The structural formula of a typical molecular sieve is $\mathrm{Me}_{z/n}(\mathrm{AlO}_2)_y \bullet \mathrm{mH_2O}$, 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 Porapack Q, Porapack 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.

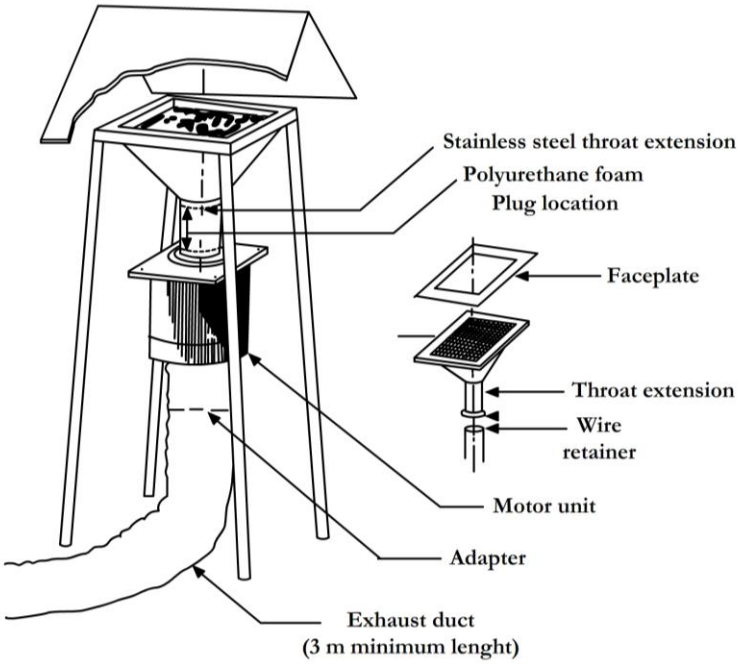

Figure 6-5. Assembled sampler and shelter with exploded view of the filter holder.

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 Detention (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.

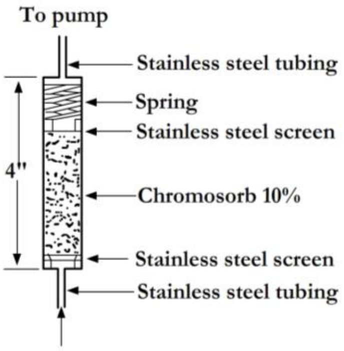

Figure 6-6. High-speed organic vapor collector.

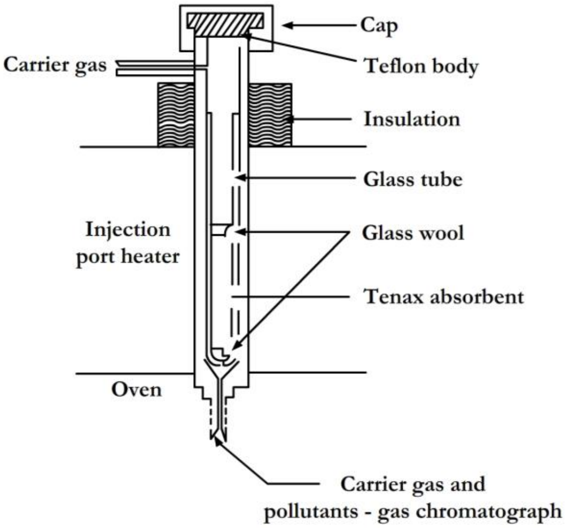

Figure 6-7. Desorption of pollutants from a Tenax-GC cartridge.

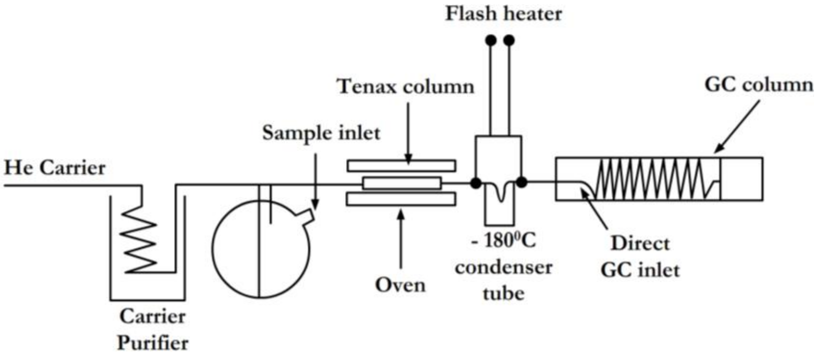

Figure 6-8. Dynamic enrichment on adsorption column (experimental setup).

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 α is given by:

(Eq. 6-7)

$$\alpha = \frac{V_o}{(V)(p)}$$

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_2	He	N_2	O_2	CO	CO_2	NO	H_2S	NH_3
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_2 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.

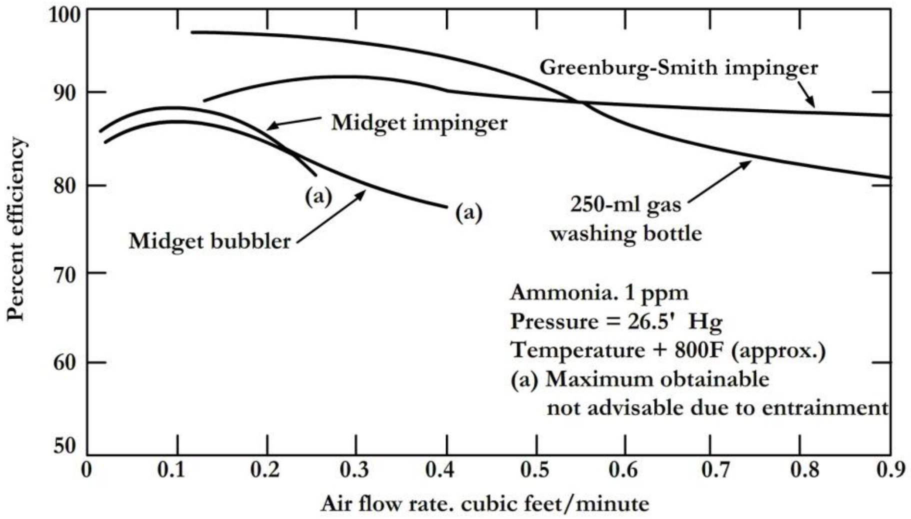

Figure 6-9. Performance curves - commercially available absorbers.

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 l 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:

(Œq. 6-10) $$p = Np_{\circ}$$

Where:
p = *partial pressure of gas to be dissolved (atm)*
N = *mole fraction of gas*
$p_{\circ}$ = *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:

$$N = \frac{p}{p_{\circ}} = \frac{1}{42} = 0.024$$

since p is 1 atm and p_o 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:

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

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).

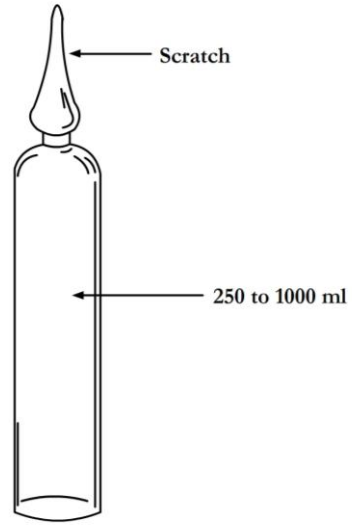

Figure 6-10. Vacuum tube.

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:

(Eq. 6-12)
$$V_2 = V_f - V_z$$

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

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

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.

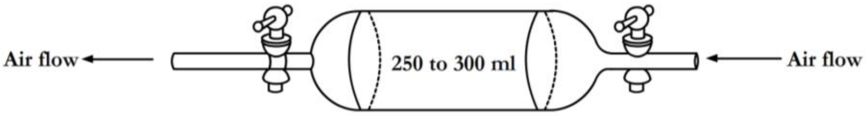

Figure 6-12. Gas-displacement collector.

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).

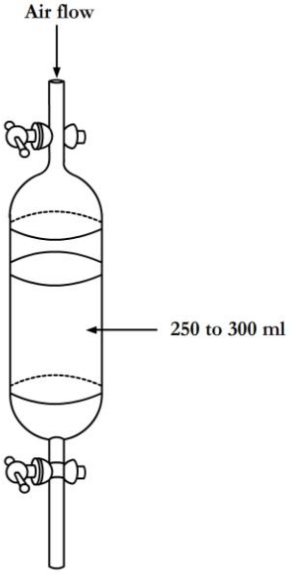

Figure 6-13. Liquid-displacement collector.

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.

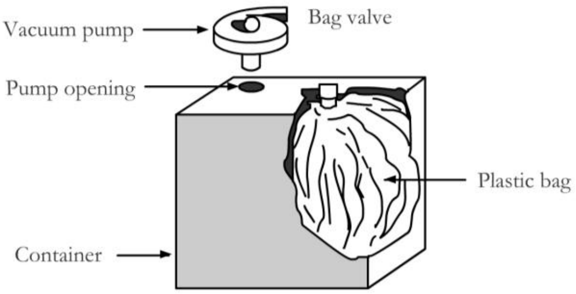

Figure 6-15. Inflation sampler.

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

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

Sampling Applications	Ambient/indoor air, soil/landfill gas, stationary sources	Ambient/indoor air, soil/landfill gas, stationary sources
"Sensitivity"	"ppbv device"	"ppmv device"
Advantages	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°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).

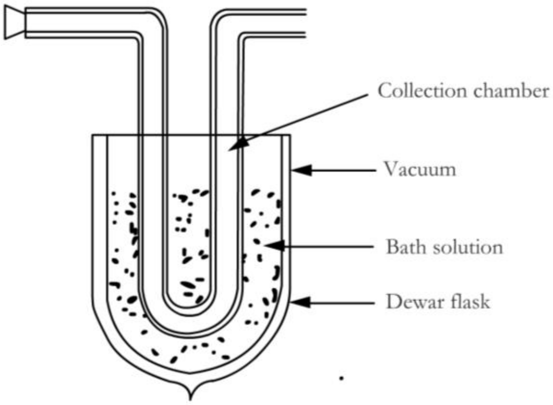

Figure 6-16. Freezeout unit.

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.

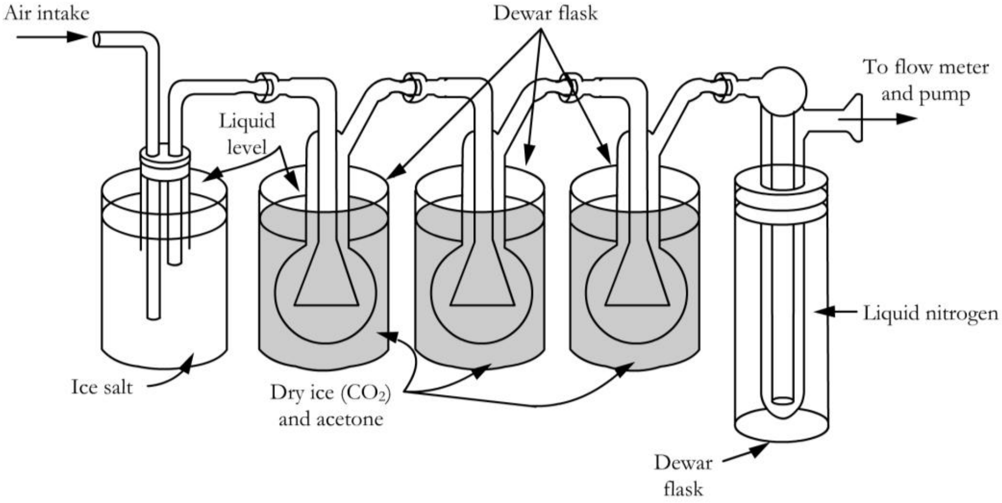

Figure 6-17. Freezeout equipment for atmospheric sample (horizontal sampling train).

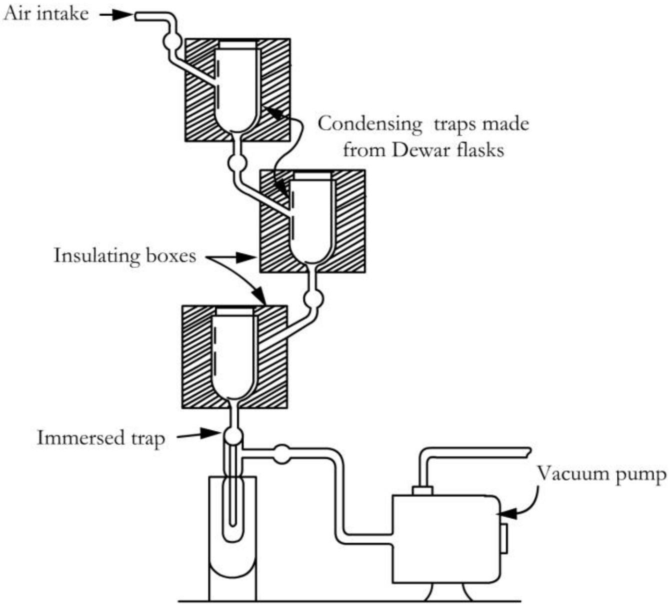

Figure 6-18. Freezeout equipment for atmospheric samples (vertical sampling train).

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.

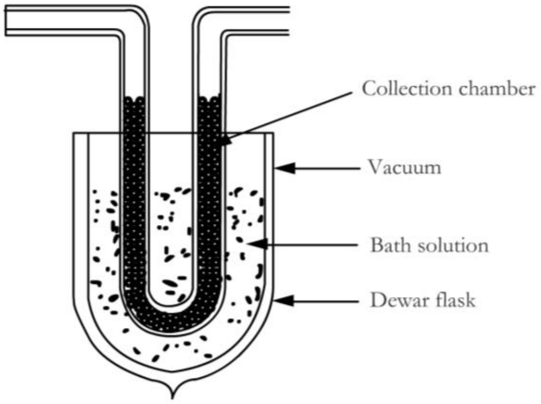

Figure 6-19. Freezeout unit showing packing material.

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°C) will condense when liquid nitrogen (B.P. = − 196°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 -10ºC to 200ºC 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 value 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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Chapter

7

Standard Methods for Criteria Pollutants

This chapter will take approximately 30 minutes to complete.

OBJECTIVES

Terminal Learning Objective

At the end of this chapter, the student will be able to identify the standard methods for criteria pollutants.

Enabling Learning Objectives

7.1 Define NAAQS.
7.2 Identify the standard reference test methods for criteria pollutants.

7.1 Introduction

To protect the public health from harmful air pollution, the 1970 Amendments to the Clean Air Act (CAA) authorized the U.S. Environmental Protection Agency (EPA) to specify national ambient air quality standards (NAAQS). The NAAQS regulate ambient concentrations of criteria pollutants as outlined in "National Primary and Secondary Ambient Air Quality Standards," Part 50 of Chapter 40 of the Code of Federal Regulations (40 CFR 50). States may choose to adopt either the NAAQS or more stringent standards.

To demonstrate compliance with the NAAQS, a network of air monitoring stations are operated nationwide. These stations test the ambient air and report the results to EPA. To ensure nationwide uniformity of these results, EPA established reference test methods for use in this network of stations. These methods are detailed in the appendices to 40 CFR 50.

7.2 Reference Method and Equivalent Method

A reference method uses a measurement principle specified in one of the appendices to 40 CFR 50. An equivalent method is a method which uses a different measurement principle, but which achieves a high degree of correlation to the reference method.

The responsibility for reviewing applications, designating reference and equivalent methods, and approving modifications resides with the Reference and Equivalent Methods (R&E) Program. Currently, this Program is part of the EPA's Office of Research and Development of the National Exposure Research Laboratory (NERL).

Reference and equivalent methods designated by the R&E Program may be either manual or automated. If a manual method is to be considered for equivalent designation, it must demonstrate a consistent relationship to the reference method when both methods are used to measure pollutant concentrations in a real atmosphere.

The distinction between automated reference and equivalent methods is based on the *measurement principle* that an instrument employs. For example, the reference measurement principle for automated methods for the detection of the oxides of nitrogen is based on the chemiluminescent reaction of nitric oxide with ozone. Any instrument, therefore, which meets the performance specification for automated methods and uses a chemiluminescent reaction of nitric oxide with ozone for detection is a reference method. Instruments using other measurement principles would be designated equivalent methods, provided they meet the performance specifications. The exception is $PM_{2.5}$ methods, where certain parts of the sampling device must be identical to the Federal specifications in form and function, as well as performance.

This section is designed to provide a brief overview of the reference methods as they are described in the Code of Federal Regulations, and discuss potential problem areas and some quality assurance considerations from a practical standpoint. With the exception of sulfur dioxide (see below), equivalent methods are not discussed in detail in this section.

Criteria Pollutants and Measurement Methods

The United States has established National Ambient Air Quality Standards (NAAQS) for six pollutants. These standards have been promulgated by the US Environmental Protection Agency (EPA) to protect public health and welfare.

There are two types of NAAQS: primary and secondary. Primary standards are designed to protect public health, while secondary standards protect public welfare, including effects of air pollution on vegetation, materials, and visibility. These pollutants and standards are listed in Table 7-1.

Table 7-1. National Ambient Air Quality Standards (NAAQS).

Pollutant	Primary Standards		Secondary Standards		Reference Method/Principle	Typical Method/Principle
	Level	Avg. Time	Level	Avg. Time		
Carbon Monoxide	9 ppm (10 mg/m^3)	8-hour(1)	None		Nondispersive infrared photometry	same
	35 ppm (40 mg/m^3)	1-hour(1)				
Lead	1.5 $\mu g/m^3$	Quarterly Average	Same as Primary		High-volume sampling with AA analysis	same
Nitrogen Dioxide	0.053 ppm (100 $\mu g/m^3$)	Annual (Arithmetic Mean)	Same as Primary		Gas-phased chemiluminescence	same
Particulate Matter (PM_{10})	150 $\mu g/m^3$	24-hour(2)	Same as Primary		High- or low-volume Sampling	same
Particulate Matter ($PM_{2.5}$)	15.0 $\mu g/m^3$	Annual(3) (Arithmetic Mean)	Same as Primary		Low-volume sampling	same
	35 $\mu g/m^3$	24-hour(4)	Same as Primary			
Ozone	0.075 ppm (2008)	8-hour(5)	Same as Primary		Gas-phased chemiluminescence with ethylene	UV photometry
	0.08 ppm (1997)	8-hour(6)	Same as Primary			
	0.12 ppm	1-hour(7) (Applies only in limited areas)	Same as Primary			
Sulfur Dioxide	0.03 ppm	Annual (Arithmetic Mean)	0.5 ppm (1300 $\mu g/m^3$)	3-hour(1)	Pararosaniline method	UV fluorescence
	0.14 ppm	24-hour(1)				

(1) Not to be exceeded more than once per year.

(2) Not to be exceeded more than once per year on average over 3 years.

(3) To attain this standard, the 3-year average of the weighted annual mean $PM_{2.5}$ concentrations from single or multiple community-oriented monitors must not exceed 15.0 $\mu g/m^3$.

(4) To attain this standard, the 3-year average of the 98th percentile of 24-hour concentrations at each population-oriented monitor within an area must not exceed 35μg/m3 (effective December 17, 2006).

(5) To attain this standard, the 3-year average of the fourth-highest daily maximum 8-hour average ozone concentrations measured at each monitor within an area over each year must not exceed 0.075 ppm (effective May 27, 2008).

(6) (a) To attain this standard, the 3-year average of the fourth-highest daily maximum 8-hour average ozone concentrations measured at each monitor within an area over each year must not exceed 0.08 ppm.

(b) The 1997 standard—and the implementation rules for that standard—will remain in place for implementation purposes as EPA undertakes rulemaking to address the transition from the 1997 ozone standard to the 2008 ozone standard.

(7) (a) The standard is attained when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 ppm is ≤ 1.

(b) As of June 15, 2005, EPA revoked the 1-hour ozone standard in all areas except the 8-hour ozone nonattainment Early Action Compact (EAC) Areas.

The national monitoring networks used to determine compliance with these NAAQS must use methods approved through the R&E Program. Following is a brief discussion regarding each of these pollutants and its associated reference method.

Particulate Matter

$PM_{2.5}$

The reference method for $PM_{2.5}$ provides for the measurement of the mass concentration of fine particulate matter having an aerodynamic diameter less than or equal to a nominal 2.5 μm in ambient air. The method requires sampling over a 24-hour period for purposes of determining whether the primary and secondary NAAQS are met.

An electrically powered air sampler draws ambient air at a constant volumetric flow rate into a specially shaped inlet and through an inertial particle size separator (impactor) where the suspended particulate matter in the $PM_{2.5}$ range is separated for collection on a polytetrafluoroethylene (PTFE) filter over the specified sampling period. Alternatively, the Very Sharp Cut Cyclone (VSCC) particle size separator may be used in place of the inertial impactor. Samplers which utilized the VSCC were initially designated as equivalent methods. In recent years they have been re-designated with reference method status.

Each filter is weighed (after moisture and temperature conditioning) before and after sample collection to determine the net gain due to collected $PM_{2.5}$. The total volume of air sampled is determined by the sampler from the measured flow rate (at actual ambient temperature and pressure) and the sampling time. The mass concentration of $PM_{2.5}$ in the ambient air is computed as the total mass of collected particles in the $PM_{2.5}$ size range divided by the actual volume of air sampled, and is expressed in micrograms per cubic meter of air ($\mu g/m^3$).

The problems with this method are the nonuniformity of sampling flow rate, artifact formation of sulfates and nitrates, loss of volatiles, filter handling errors, hygroscopic particulate matter, nonsampled particulate matter, and timing errors.

A more detailed discussion of $PM_{2.5}$ samplers can be found in Chapters 4 and 5 of this manual.

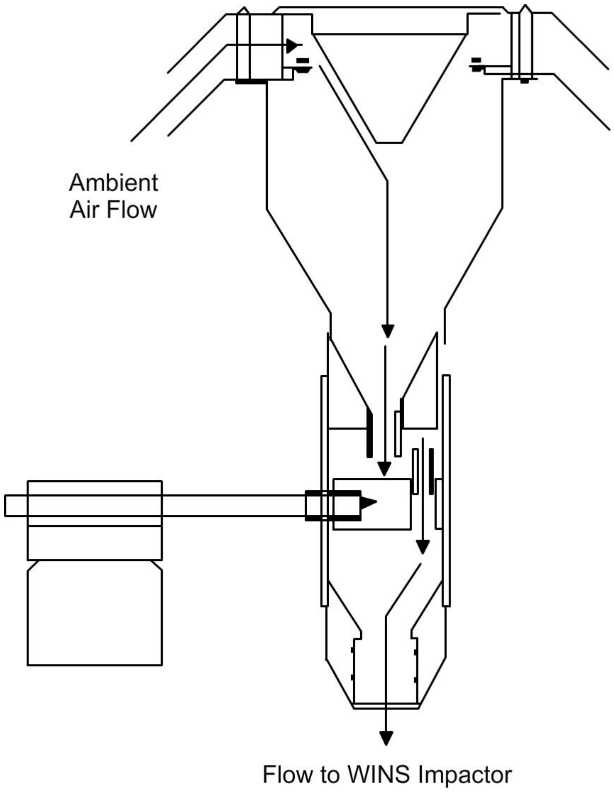

Figure 7-1. Schematic image of $PM_{2.5}$ sampler utilizing a WINS impactor.

PM_{10}

The reference method for PM_{10} provides for the measurement of the mass concentration of fine particulate matter having an aerodynamic diameter less than or equal to a nominal 10 micrometers in ambient air. The method requires sampling over a 24-hour period for purposes of determining whether the primary and secondary NAAQS are met.

An air sampler draws ambient air at a constant flow rate into a specially shaped inlet where the suspended particulate matter is inertially separated into one or more size fractions within the PM_{10} size range. Each size fraction in the PM_{10} size range is then collected on a separate filter over the specified sampling period. Some PM_{10} samplers use particle size separators which differ from the configuration shown in Figure 7-2 and are designated as reference methods. These include high- and low-volume samplers which use various inlet configurations (see 40 CFR 50, Appendix L for descriptions of these inlet configurations) based on inertial impaction and instruments known as dichotomous samplers which separate particle sizes using "virtual" impaction.

Each filter is weighed (after moisture equilibration) before and after use to determine the net weight (mass) gain due to collected PM_{10}. The total volume of air sampled, corrected to EPA reference conditions (25°C, 101.3 kPa), is determined from the measured flow rate and the sampling time. The mass concentration of PM_{10} in the ambient air is computed as the total mass of collected particles in the PM_{10} size range divided by the total volume of air sampled, and is expressed in micrograms per standard cubic meter (μg/std m^3).

The problems with this method are the nonuniformity of sampling flow rate, artifact formation of sulfates and nitrates, loss of volatiles, filter handling errors, hygroscopic particulate matter, nonsampled particulate matter, and timing errors.

A more detailed discussion of PM_{10} samplers can be found in Chapters 4 and 5 of this manual.

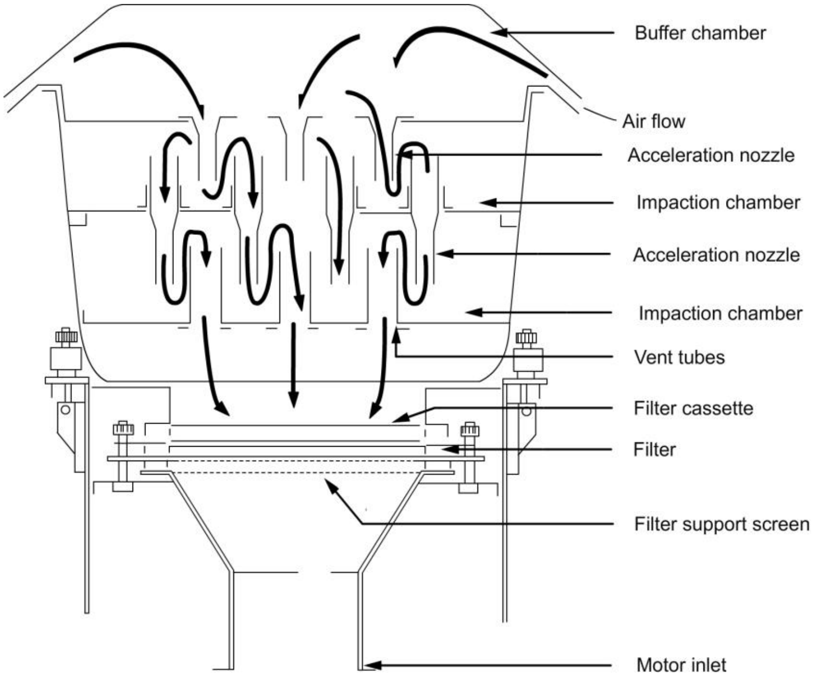

Figure 7-2. Schematic of PM_{10} sampler.

Ozone

The reference measurement principle for the measurement of ozone is the gas-phase chemiluminescence resulting from the reaction of ozone with ethylene. Ambient air and ethylene are delivered simultaneously to a mixing zone where the ozone in the air reacts with ethylene to emit light, which is detected by a photomultiplier tube. The resulting photocurrent is amplified and is either read directly or displayed on a recorder.

The unstable nature of ozone requires that ozone be generated *in situ* in order to calibrate ozone monitors. Ultraviolet (UV) photometry has been designated as the calibration procedure. A schematic of a typical UV photometric calibration system is shown in Figure 7-3.

Ozone monitoring locations now use the equivalent method, which is an ultraviolet method.

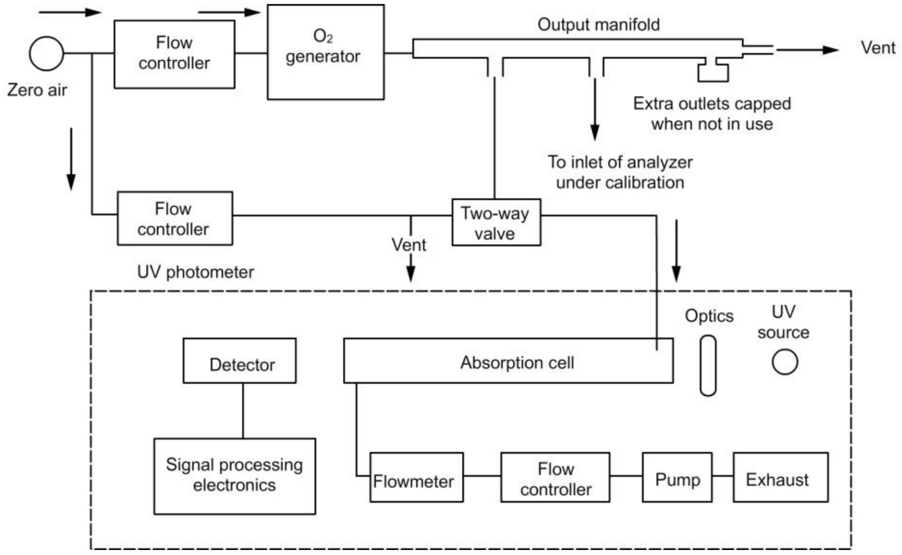

Figure 7-3. Schematic diagram of a typical photometric calibration system.

A more detailed discussion of ozone monitors and the generation of test atmospheres for their calibration can be found in the Student Manual for U.S. EPA course EPA 464: Analytical Methods for Air Quality Standards.

Carbon Monoxide

The reference measurement principle used to measure ambient levels of carbon monoxide is nondispersive infrared (NDIR) photometry. A signal is produced as a result of the infrared absorption of carbon monoxide which can be related to the absolute CO concentration by calibrating the photometer as specified in Appendix C of 40 CFR 50.

The problem areas associated with this method are the broad band absorption of carbon dioxide and water vapor. These two compounds' absorption results in an interference. The techniques of "negative filtering" or gas filter correlation alleviate these problems.

A more detailed discussion of carbon monoxide monitors and the generation of test atmospheres for their calibration can be found in the Student Manual for U.S. EPA course EPA 464: Analytical Methods for Air Quality Standards.

Nitrogen Dioxide

The reference measurement principle for the determination of nitrogen dioxide is the gas-phase chemiluminescence reaction of nitric oxide with ozone (Eq. 7-1).

(Eq. 7-1) $$NO + O_3 \rightarrow NO_2 + O_2 + hv\left(light\right)$$

Nitrogen dioxide is measured indirectly by measuring total oxides of nitrogen ($\mathrm{NO_x = NO_2 + NO}$) and electronically subtracting the nitric oxide concentration (NO), yielding a nitrogen dioxide determination (NO_2). A measure of the total oxides of nitrogen is obtained by passing the sample across a catalytic converter, which reduces nitrogen dioxide to nitric oxide (Eq. 7-2).

(Eq. 7-2) $$NO_2 + catalytic\,converter \rightarrow NO + O$$

The calibration of the NO and NO_x channels of the instrument is accomplished by diluting a pressurized tank of NO. The calibration of the NO_2 channel is accomplished with a permeation device or the gas-phase titration of an NO standard gas with ozone. The gas-phase titration involves the following reaction (Eq. 7-3):

(Eq. 7-3) $$NO + O_3 \rightarrow NO_2 + O_2$$

This produces a known amount of nitrogen dioxide which allows one to calibrate the NO_2 channel of the monitor. The other calibration procedure specified in Appendix F, 40 CFR 50, uses a dynamic dilution system in combination with a permeation device to produce a known amount of NO_2.

The problem areas associated with this method are interferences such as peroxyacetyl nitrate (PAN) and other nitrogen-containing compounds. In periods of high photochemical activity, corrections for these interferences may be necessary.

The chemical composition of the atmosphere plays an important role in determining the validity of the nitrogen dioxide measurements obtained using a reference method analyzer. For most ambient air measurements, however, interferences such as the ones mentioned previously are minimal. The frequency of calibration and other maintenance (e.g., replacement of ozone filter, check of converter efficiency, etc.) are important quality assurance considerations.

A more detailed discussion of nitrogen dioxide monitors and the generation of test atmospheres for their calibration can be found in the Student Manual for U.S. EPA course EPA 464: Analytical Methods for Air Quality Standards.

Sulfur Dioxide

The reference method for the measurement of dioxide in ambient air is a manual wet-chemical method − the pararosaniline method. Sulfur dioxide is bubbled through a solution of potassium tetrachloromercurate (TCM) which forms a monochlorosulfonatomercurate complex. This complex forms an intensely colored solution upon addition of pararosaniline dye and formaldehyde. The concentration of sulfur dioxide can be determined spectrophotometrically by measuring the absorbance of the colored solution.

The potential problems associated with interferences are minimized by the procedures listed in Table 7-2.

Table 7-2. Parasaniline interferences.

Interference	Corrective procedure
Ozone	Time delay
Heavy metals	Addition of EDTA and phosphoric acid
Oxides of nitrogen	Addition of sulfamic acid

Other precautions to be considered related to the sampling train (Figure 7-4) and to sampling conditions. The inner diameter of the tip of the impinger stem should be checked to make sure that a No. 79 jeweler's drill bit will pass through, but a No. 78 jeweler's drill bit will not. The temperature instability of the monochlorosulfonatomercurate complex during sampling also poses potential problems. This is minimized by using a temperature control device to maintain a temperature of 15° ± 10°C during sampling. Collected samples must be kept at a temperature of 5° ± 5°C. Since this method involves a laboratory analysis of the sample after collection in the field, care should be taken in handling the sample once it has been collected to avoid contamination.

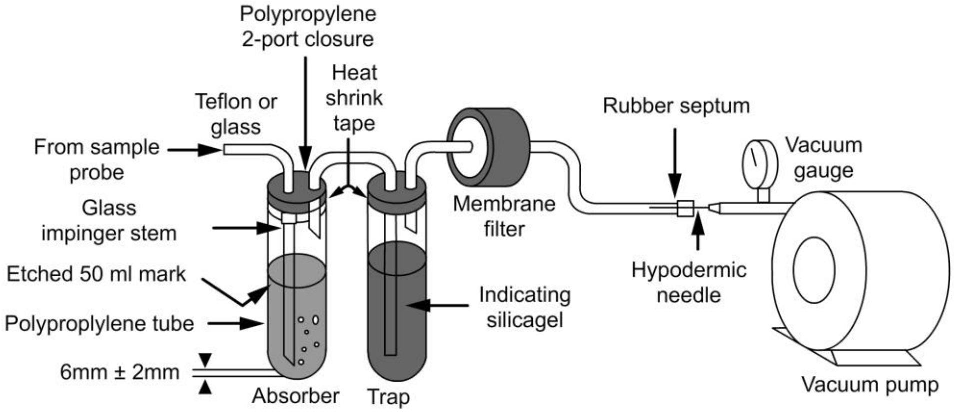

Figure 7-4. SO_2 sampling train for 24-hour sampling.

Current monitoring sites do not use the reference method for sulfur dioxide sampling. A continuous equivalent method based on ultraviolet (UV) fluorescence is used nearly exclusively today. A signal is produced as a result of a SO_2 molecule emitting a characteristic wave length of light (fluorescence) as it returns to a lower "energy state" after having been "electronically excited" by radiation of UV energy. The fluorescence emissions are measured by a detector and processed electronically to yield the concentration of SO_2 in the sample air.

The problem areas associated with UV fluorescence are related primarily to the quenching effects of O_2, N_2, CO_2, and water vapor. For ambient monitoring, the levels of O_2, N_2, and, for the most part, CO_2 and water vapor are constant; thus the quenching effect is fairly constant. Hydrocarbons may also interfere, but all equivalent method analyzers are equipped with a hydrocarbon scrubber (i.e., "kicker" or "cutter") to eliminate this potential problem.

A more detailed discussion of sulfur dioxide monitors and the generation of test atmospheres for their calibration can be found in the Student Manual for U.S. EPA course EPA 464: Analytical Methods for Air Quality Standards.

Lead

The reference method for lead consists of measuring the lead content of particulate matter collected by the total suspended particulate reference method's high-volume sampling procedure as described below. After sample collection, lead is acid-extracted from the particulate matter of a ¾ in. x 8 in. strip of the high-volume filter. Finally, the lead content of the resulting solution is determined by atomic absorption spectrometry.

In the high-volume method, air is drawn through a filter composed of glass fibers or other relatively inert, nonhygroscopic material, and the amount of particulate matter collected is determined gravimetrically. A flow rate measurement device for the sampler is calibrated against actual air flow with a flow rate transfer standard, which is first calibrated against a positive displacement standard volume meter.

The problems with this method are the nonuniformity of sampling flow rate, artifact formation of sulfates and nitrates, loss of volatiles, filter handling errors, hygroscopic particulate matter, nonsampled particulate matter, timing errors, recirculation of sampler exhaust, and the wind direction sensitivity of the sampler.

Potential problems exist in the analysis portion of the method as well. In addition to the sampling problems associated with the high-volume method, lead may be distributed nonuniformly across the filter. The problem can be alleviated by analyzing a larger portion of the filter. Chemical and light-scattering interferences may be encountered during the atomic absorption spectrophotometric analysis. Chemical interferences can be overcome using the method of standard additions. Light-scattering interferences can be corrected using a dual-channel atomic absorption spectrophotometer equipped with a continuum light source, by using a nonabsorbing wavelength that is near the lead analytical wavelength, or by using a chelating agent to chemically isolate potential interferences during the analysis so that they do not interfere. Furthermore, for accurate particulate lead analyses, it is necessary that the variation of lead content from filter to filter within a given batch of blank filters be small.

A more detailed discussion of lead monitors can be found in Chapters 4, 5, and 8 of this manual.

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Chapter 8

This chapter will take approximately 1 hour to complete.

Introduction to Ambient Air Sampling for Air Toxics

OBJECTIVES

Terminal Learning Objective

At the end of this chapter, the student will be able to describe ambient air sampling for air toxics.

Enabling Learning Objectives

8.1 Define *toxic air pollutants*.

8.2 Describe risk assessment and risk characterization.

8.3 Describe the air toxics methods for the air toxics monitoring program.

8.1 Introduction

What are Toxic Air Pollutants?

Toxic air pollutants are poisonous substances in the air that come from natural sources (such as radon gas coming up from the ground) or from manmade sources (such as chemical compounds given off by factory smokestacks) and can harm the environment or your health. Inhaling toxic air pollutants can increase your chances of experiencing health problems. For example, inhaling the benzene fumes that are given off when you pump gas into your car can increase your chances of experiencing health effects that have been associated with exposure to benzene, such as leukemia.

Some air toxics are also involved in the formation of other pollutants, principally ozone and particulate matter (PM). If we can significantly reduce volatile organic compounds (VOCs), this will not only help with air toxics risk, but also help reduce ozone and PM formation.

Here are some more facts about air toxics:

- Air toxics are also known as hazardous air pollutants (HAPs).
- These pollutants are known or suspected to cause cancer or other serious health effects.
- The principle pathway for most HAPs is inhalation.
- High concentration locales are often heavily industrialized areas.
- Analysis of ambient air monitoring data can be an effective means of assessing air quality and associated potential health risks, and assessing trends and regulatory program effectiveness.

Several technical tools have been developed to help EPA and their partners in the state, local, and academic communities. These tools include emission inventories, air quality modeling, data analysis, and monitoring programs. The models, inventories, and data analyses are the planning and assessment tools that directly support numerous assessments across the air toxics programs. The first National Scale Air Toxics Assessment (NSATA, also known as "1996 NATA") provided county level summaries of HAP exposures based predominantly on modeling and emissions data from the year 1996. Monitoring data indirectly—and, in some cases, directly—support all the technical tools as well as the larger programs. The challenge faced in monitoring for air toxics is effectively marrying observations with these program elements.

Clean Air Act of 1990

In 1990, the United States promulgated the Clean Air Act (CAA) of 1990. This was major landmark legislation on many levels. For the first time, air toxics were regulated. Section 112 of the Clean Air Act states the powers that the federal government has in regulating, monitoring, and reducing HAPs within the country. Section 112 originally listed 189 HAPs. However, because one was de-listed, currently the CAA recognizes 188 listed HAPs. Figure 8-1 shows the breakdown of the makeup of the HAPs listed in Section 112.

As can be seen from Figure 8-1, well over half of the HAPs listed in the Clean Air Act are volatile compounds, or VOCs. These are a class of compounds that *volatilize* in normal ambient conditions. *Volatile* means that they are in the gaseous phase. Semi-volatile compounds (SVOCs) are compounds of a molecular weight such that their volatility is dependent on the temperature and pressure of the atmosphere. For instance, the compound naphthalene is considered to be a SVOC. Compounds such as naphthalene can be solid, liquid, or gas phase depending on ambient conditions. At higher atmospheric temperatures, naphthalene acts like a gas. However, in colder times of the year, naphthalene is a solid. Non-volatile compounds are those that are never gaseous in ambient air, such as particulate matter or particles. Particles in the air can contain HAP compounds, such as arsenic, cadmium, or lead.

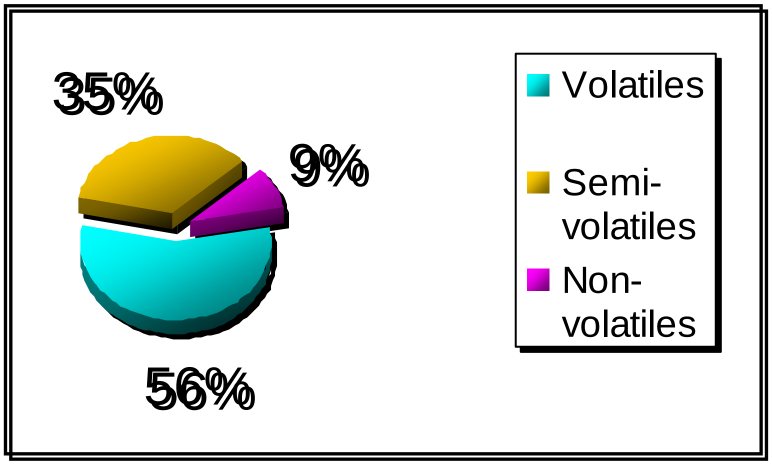


Figure 8-1. Breakdown of HAPs by class.

Timeline for Air Toxics Monitoring

Figure 8-2 illustrates the timeline for the development of air toxics monitoring in the United States. The 1990 CAA amendments provide the framework for the air toxics program. The air toxics program is designed to characterize, prioritize, and equitably address the serious impacts of HAPs on public health and the environment through a strategic combination of regulatory approaches, voluntary partnerships, ongoing research and assessments, and education and outreach. In addition to promulgating Section 112 for HAPs, the CAA also created a program in the early 1990s known as the Photochemical Assessment Monitoring Stations (PAMS) program. The PAMS program called for the measurement of VOCs that are highly reactive and can lead to the formation of ozone. Many VOCs that are HAPs are also reactive. For example, benzene, formaldehyde, and 1,3-butadiene are both PAMS compounds and HAPs. Two methods were developed by the EPA to measure these compounds: Toxic Organics (TO) 11 and TO-14. Both of these methods were useful in developing updated methods: TO-11A and TO-14A.

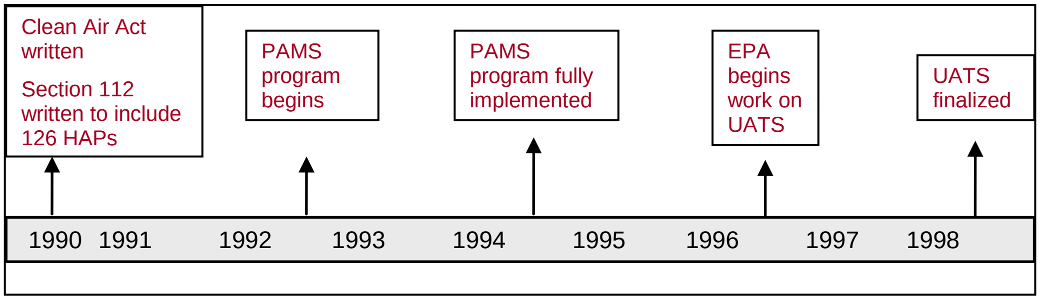


Figure 8-2. Timeline for air toxics monitoring, 1990 to 2000.

In 1996, the EPA started work on the Urban Air Toxics Strategy (UATS). The major components of the Integrated Urban Air Toxics Strategy (standards, risk initiatives, air toxics assessments, and educational outreach) are the same as the major components of our overall national air toxics program. The EPA is continuing to develop a number of national standards for stationary and mobile sources as a part of the national air toxics program. These standards, as well as standards developed by state and local authorities, are expected to improve air quality in urban and rural areas. As part of the national air toxics program, we will be assessing what additional actions, both at the national and local level, are needed to further improve air quality. The UATS complements the existing national efforts by focusing on achieving further reductions in air toxics emissions in urban areas. The UATS includes state and local governments particularly in planning UATS activities and other initiatives under the national air toxics program to assess and address local air quality concerns. The UATS was finalized in 1998.

The EPA and its partners cannot monitor everywhere. So, in order to better understand public exposure, the EPA has created the National Air Toxics

Assessment (NATA). The NATA helps us identify areas of concern, characterize risks, and track our progress toward meeting our overall air toxics program goals. NATA activities include expansion of air toxics monitoring, improvements and periodic updates to emissions inventories, national- and local-scale modeling of air quality and exposure, continued research on health effects and exposures to both ambient and indoor air, and development and use of improved risk and exposure assessment tools.

Figure 8-3 illustrates the development of several air toxics monitoring programs. From 1998, EPA and its stakeholders worked together to create the Air Toxics Concept Paper. It established the framework for future monitoring throughout the United States. The monitoring network should be incrementally designed to first address the highest priority needs of the air toxics program: to focus on pollutants and sources which pose the greatest risk to the largest number of people and the greatest risk to the environment. Because of limited knowledge in measuring many of the 188 HAPs, the program should initially focus on those pollutants that EPA, state, and local agencies have identified as having the most significant potential health impacts and routine measurement methods. The list of HAPs in the UATS is a logical starting point. Several UATS pollutants are also important from an ecosystem risk assessment perspective. As additional priority air toxics are identified and as monitoring capabilities improve, additional HAPs can be added to the monitoring program.

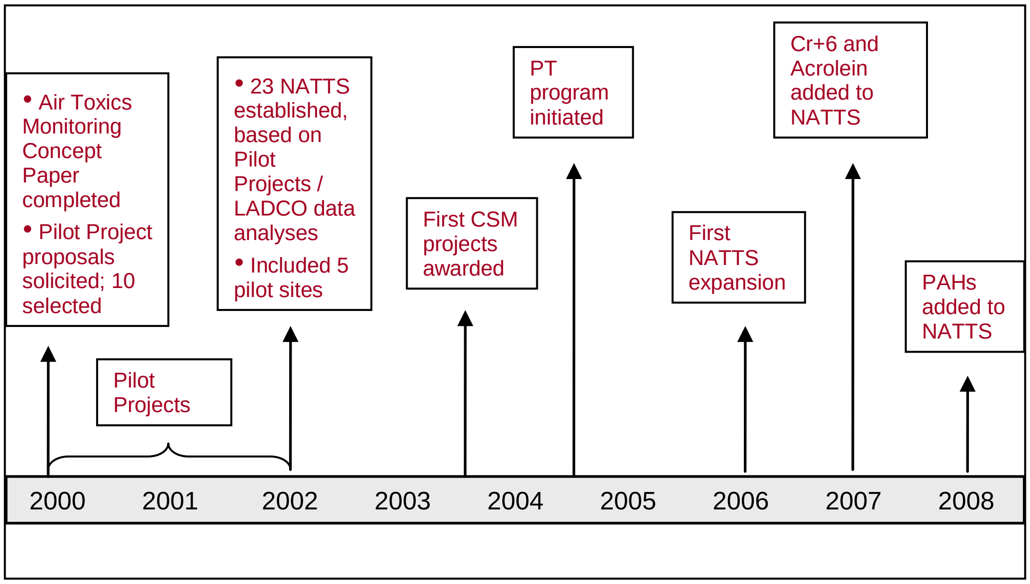


Figure 8-3. Timeline for air toxics monitoring, 2000 to 2008.

This is not to say that all UATS HAPs must be measured at all locations and that non-UATS HAPs should not currently be measured at some locations. To permit comparisons among HAPs and to facilitate dispersion and deposition model evaluation, however, some number of "core" UATS HAPs should be initially measured at a number of locations nationwide. The HAPs measured should include those associated with the highest toxicity-weighted emissions or those that are judged responsible for a large percentage of the risk associated with exposures to ambient air toxics. Similarly, as many UATS HAPs as possible should be measured at an agreed upon, albeit initially small, number of comprehensive monitoring locations. Such comprehensive platforms should be selected to reflect a broad representative mix of UATS HAP emissions. As monitoring capabilities improve and available resources increase, the list of compounds and locations can change.

The outcome of the Air Toxics Concept Paper was to create a Pilot Project. The EPA funded and worked with the regional offices to establish 10 sites throughout the country to pilot a national network. Pilot Project sites would be operated by state and local government agencies, but overseen by the EPA and its regional partners. The Pilot Project stations operated for 1–2 years and gave its partners valuable information about level of detection, day-to-day variability, operating procedures, and quality assurance. The compounds selected were confirmed by earlier conclusions from the 1996 NATA and prevailing judgment, and illustrated the variant nature of air toxics both within and across cities. With the exception of relatively consistent motor vehicle signals, the data showed extreme variation in the relative levels of particular pollutants that largely were influenced by proximity to sources.

Once the Pilot Project was over, EPA and its partners began planning for a long-term, fixed network that would allow us to understand trends. Thus the National Air Toxics Trends Stations (NATTS) were proposed in 2002. Information from the Pilot Project illustrated that a single trends site should rarely be viewed as being representative of the many disparate locations throughout a metropolitan area. Accordingly, a more realistic expectation of the NATTS emerged, suggesting that these sites should adequately track the progress of mobile-source-oriented emission reduction programs at a national level, but provide only a limited perspective on characterizing a city's air quality. More focused studies that either address fairly specific source categories or provide greater spatial resolution (i.e., more stations) are needed to complement the NATTS.

It was decided that more in-depth studies would be needed rather than a long-term trends network. Therefore, EPA initiated the Community Scale Monitoring (CSM) projects in 2003. The CSM projects are intense, focused monitoring projects that look to answer specific questions about HAPs in an area or city and understand the risk and exposure of the population to those specific HAPs.

8.2 What is Risk?

Health risks, put simply, are a measure of the chance that you will experience health problems. Exposure to toxic air pollutants can increase your health risks. For example, if you live near a factory that releases cancer-causing chemicals and you inhale contaminated air, your risk of getting cancer can increase. Risk is defined as function of exposure and toxicity as stated in the following equation:

RISK = f [(Measure of Exposure) (Measure of Toxicity)]

Exposure to HAPs can come in many forms. HAPs are released into the atmosphere from factories, our automobiles, and other processes. HAPs disperse into the atmosphere and can be affected by local and long distance meteorology. HAPs can deposit into lakes, oceans, and streams by wet deposition in the form of rain or snow. Dry deposition of HAPs usually occurs as SVOCs or particles. This type of deposition is considered to be "dry" because it is not associated with rainfall.

We are exposed to these compounds by three modes: ingestion, dermal, and inhalation. People uptake and intake HAPs at different rates and in different ways. Most HAPs are excreted by the body, but some are taken into target organs, which over time causes a number of health effects. Figure 8-4 illustrates the pathways and endpoints of HAPs.

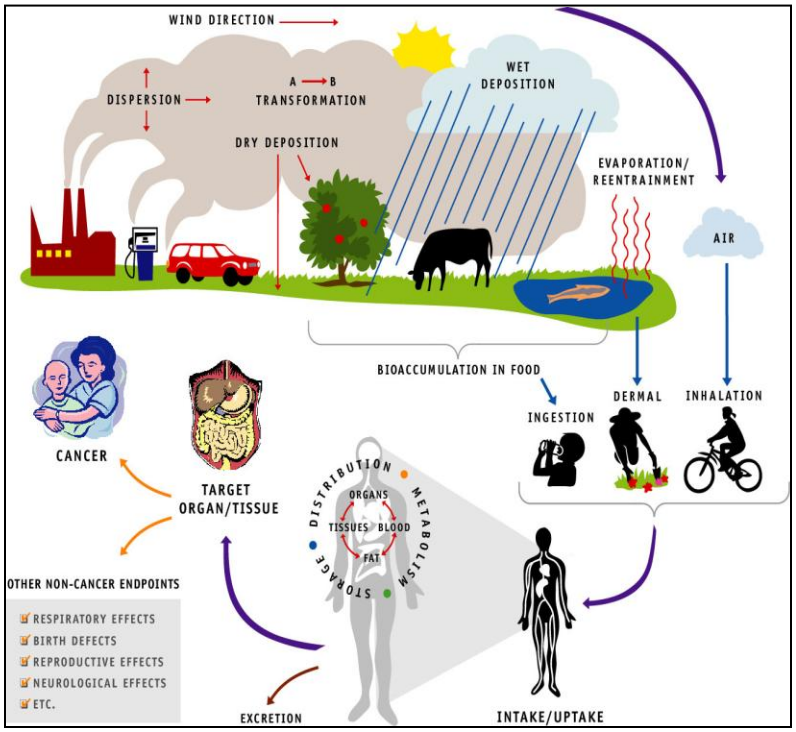


Figure 8-4. Various pathways of exposure to HAPs.

What is a Risk Assessment?

In order to understand how the public is at risk to HAPs, scientists and government officials perform risk assessments. One of several tools used in risk management, risk assessments estimate the increased risk of health problems in people. A risk assessment for a toxic air pollutant combines results of studies on the health effects of various animal and human exposures to the pollutant with results of studies that estimate the level of people's exposures at different distances from those sources (see Figure 8-5).

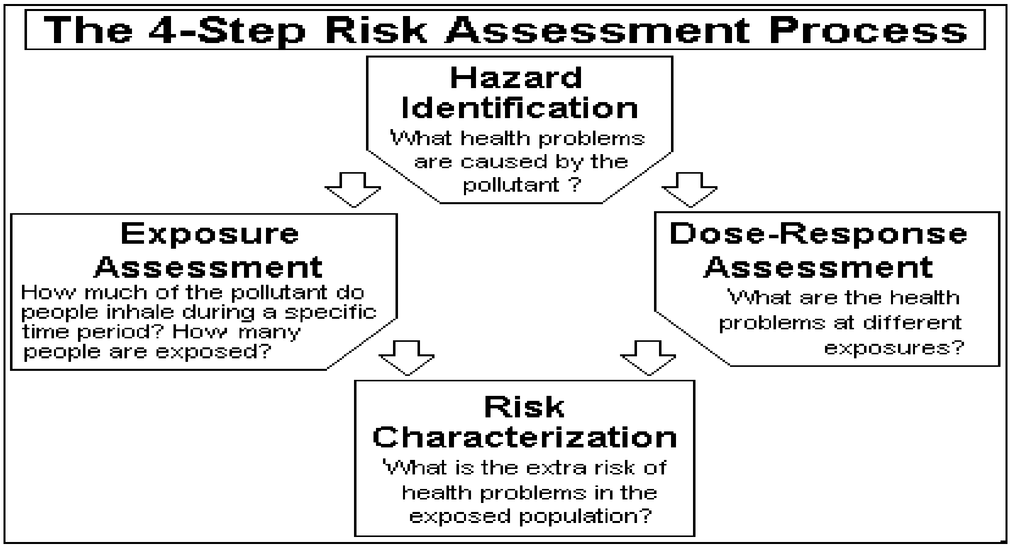


Figure 8-5. Risk assessment flow chart.

While the estimates provided by these risk assessments are far from perfect, they do help scientists evaluate the risks associated with emissions of toxic air pollutants. Using risk estimates and other factors, the government can set regulatory standards to reduce people's exposures to toxic air pollutants and thus reduce the risk of experiencing health problems.

Hazard Identification

The toxic air pollutants of greatest concern are those that cause serious health problems or affect many people. Such health problems can include cancer, respiratory irritation, nervous system problems, and birth defects. Some health problems occur very soon after a person inhales a toxic air pollutant. These immediate effects may be minor, such as watery eyes. Or they may be serious, such as life-threatening lung damage. Other health problems, such as cancer, may not appear until many months or years after a person's first exposure to the toxic air pollutant. Risk is also affected by whether exposure is acute or chronic. Acute exposure is of severe but short duration, while chronic exposure lasts for a long period of time or is marked by frequent recurrence.

Weight of Evidence for Health Problems of Concern

In hazard identification, scientists evaluate all available information about the effects of a toxic air pollutant to estimate the likelihood that a chemical will cause a certain effect in humans. The better the evidence, the more certain scientists can be that a toxic air pollutant causes specific health problems. The amount, type, and quality of evidence are all important. The best type of evidence comes from human studies. This evidence may be in the form of case reports, such as physicians' reports of an unusual number of cases of a specific illness. Other more formal studies can be done that compare the number of cases of a particular illness in groups of people with different levels of exposures (for example, cases of leukemia in rubber manufacturing workers).

Because human information is very limited for most toxic air pollutants, scientists often conduct studies on laboratory animals, such as rats. Animal studies are performed under controlled laboratory conditions. Scientists can study a variety of health effects by exposing animals to pollutants at varied concentrations and for varied time periods. When relying on animal studies only, scientists need to be satisfied that health effects in humans are likely to be the same as those in the animals tested. Scientists try to use animal species with body functions that are similar to humans.

Exposure Assessment

An exposure assessment estimates how much of a pollutant people inhale during a specific time period, as well as how many people are exposed. Because there are many possible sources of toxic air pollutants, such as a factory smokestack or thousands of automobiles crossing a busy intersection each day, the first step in an exposure assessment is to decide which sources are giving off the pollutant of concern. Once the identity and location of the source(s) are known, the next step is to determine the amounts of the toxic air pollutant released in a specific time period and how it moves away from the source(s). Scientists use either monitors or computer models to estimate the amount of pollutant released from the source and the amount of pollutant at different distances from the source. Monitors are used to sample the air and measure how much of the pollutant is present. Computer models use mathematical equations to represent the processes that occur when a facility releases a pollutant and the movement of pollutants through the air. Factors such as distance from the source to exposed persons, wind speed and direction, and smokestack height (for factories) affect these estimates.

The number of people exposed at different distances from the site of release can be estimated with computer models that use information from the census and from maps. Some models can even estimate exposures for the different places people are each day—including indoor, automobile, outdoor, and workplace exposures. The final step in an exposure assessment is to estimate the amount each person inhales. To do this, scientists combine estimates of the breathing rate and lifespan of an average person with estimates of the average amount of pollutant in that person's air.

Dose-Response Assessment

The following description applies to how HAPs enter the body, interact within the body, and are eliminated from the body. First, toxic air pollutants get into the body mainly through breathing. They can also be ingested (for example, children eating soil contaminated with lead) or absorbed through the skin. Once a pollutant enters the body, it can stay in the lungs (like asbestos), be exhaled, or move into the blood from the lungs (like the oxygen we breathe) or from the digestive system or skin. In the blood it is carried to all parts of the body. As it moves around the body, a pollutant can undergo chemical changes, especially as it passes through the liver, becoming less, or more, toxic. Finally, the pollutant can be exhaled, it can leave the body in urine, bowel movements, sweat, or breast milk, or it can be stored in hair, bone, or fat.

Toxic air pollutants can cause health problems by interfering with normal bodily functions. Most commonly they change chemical reactions within individual cells, the building blocks of living things. These changes can kill cells, impair cell function, or redirect cell activity. The results can be damaged organs, birth defects when the cells of an unborn child are damaged, or cancer that develops when cells begin to grow at an uncontrolled rate.

Dose-Response Relationships

The dose-response relationship for a specific pollutant describes the association between exposure and the observed response (health effect). In other words, it estimates how different levels of exposure to a pollutant change the likelihood and severity of health effects. Just as in hazard identification, scientists use results of animal and human studies to establish dose-response relationships.

Dose-response relationship for cancer: In the absence of clear evidence to the contrary, EPA assumes that there are no exposures that have "zero risk" -- even a very low exposure to a cancer-causing pollutant can increase the risk of cancer (albeit a small amount). EPA also assumes that the relationship between dose and response is a straight line -- for each unit of increase in exposure (dose), there is an increase in cancer response.

Dose-response relationship for noncancerous effects: A dose may exist below the minimum health effect level for which no adverse effects occur. EPA typically assumes that at low doses the body's natural protective mechanisms repair any damage caused by the pollutant, so there is no ill effect at low doses. However, for some substances, noncancerous effects may occur at low doses. The dose-response relationship (the response occurring with increasing dose) varies with pollutant, individual sensitivity, and type of health effect.

Risk Characterization

Information is presented in different ways to illustrate how individuals or populations may be affected. Some of the most common risk measures are described here. Combining the results of the exposure assessment and the dose-response assessment gives an estimate of the increased lifetime risk of cancer for an individual exposed to the maximum predicted long-term concentration.

$$\text{Maximum Lifetime Exposure} \times \text{Dose-Response Relationship} = \text{Maximum Individual Lifetime Risk}$$

Many people may be exposed to less than the maximum level. Depending on the amount of exposure, an individual's risk of cancer will vary. The distribution of individual risk is usually expressed as the number of people estimated to be at various levels of risk. Distributions of individual risk are used to calculate population risk. The population cancer risk is usually expressed as the expected increased incidence of cancer (that is, the number of new cases each year) for all people exposed to the pollutant. For example, the estimated population cancer risk may be the number of new cancer cases per year expected among residents within 30 miles of a certain large source. Health reference levels refer to exposure levels that will not cause significant risks of noncancerous health effects. Long-term exposure to levels below these levels are assumed to produce no ill effects.

Health reference levels are an example of one index that government agencies use in characterizing noncancerous health risks. These levels are generally developed from exposure levels that do not produce ill effects in experimental animals. These exposure levels are adjusted to account for animal-human differences (such as breathing rate) and for underlying uncertainties (such as the difference in sensitivity between healthy adults and more sensitive people like children and the elderly). Risk analysts then compare the health reference levels with the exposure estimates to determine how many people are exposed to concentrations higher than the health reference level. Some of these people might experience ill effects.

Although scientists can estimate risks caused by toxic air pollutants in animals experimentally or in humans who have unusual exposures, converting these estimates to those expected in people under a wide range of conditions is difficult and can be misleading. By their nature, risk estimates cannot be completely accurate. The main problem is that scientists don't have enough information on actual exposure and on how toxic air pollutants harm human cells. The exposure assessment often relies on computer models when the amount of pollutant getting from the source(s) to the people can't be easily measured. Dose-response relationships often rely on assumptions about the effects of pollutants on cells for converting results of animal experiments at high doses to human exposures at low doses. When information is missing or uncertain, risk analysts generally make assumptions that tend to prevent them from underestimating the potential risk -- that is, these assumptions provide a margin of safety.

8.3 Introduction to Air Toxics Methods

Monitoring Program Goal and Objectives

The goal of the air toxics monitoring program is to support reduction of public exposure to HAPs. Monitoring data will provide a critically important role by characterizing HAP concentrations to support three very basic monitoring objectives, and also several sub-objectives. These objectives are:

- *Trends:* Measurements of key HAPs in representative areas of the nation provide a basic measure of air quality differences across cities and regions and over time in specific areas. Trends measurements provide one basis for accounting for program progress.

- *Exposure Assessments*: Ambient measurements may serve as a surrogate for actual human exposure. However, understanding the relationships between ambient concentrations and personal exposure, and how human activities impact these relationships, is critical for true exposure assessments. Therefore, ambient measurements *support* exposure assessments by providing ambient concentration levels. In addition, ambient measurements may also provide direct input into more detailed human exposure models that can be used to estimate actual human exposures.
- *Air Quality Model Evaluation:* Measurements provide basic ground truthing of models which in turn are used for exposure assessments, development of emission control strategies, and related assessments of program effectiveness. In addition, measurements provide direct input into source-receptor models, which provide relatively direct linkage between emission sources and receptor locations.

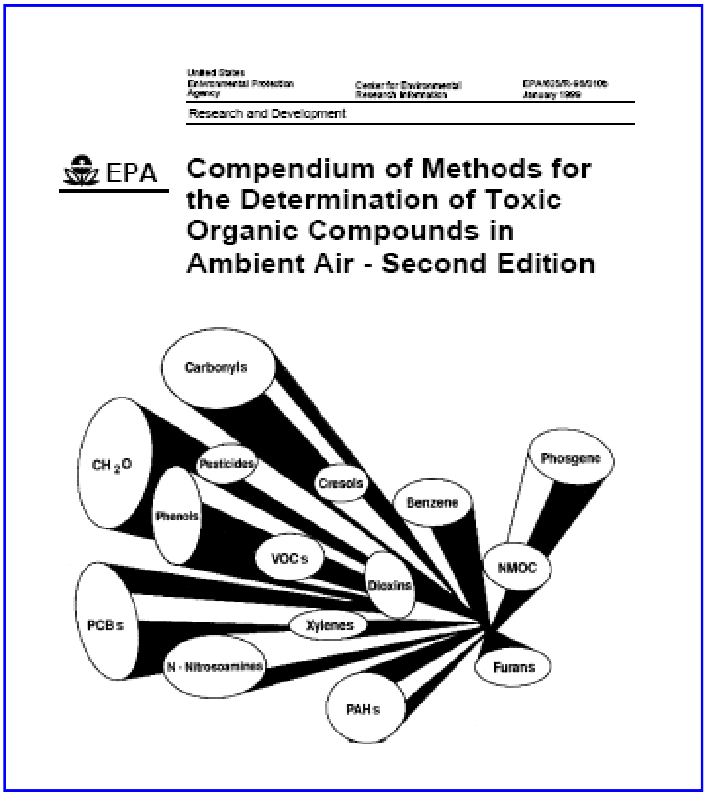
Sub-objectives to aid the overall program in general, and state and local jurisdictions in particular, are as follows:

- *Program Accountability:* Monitoring data provide perhaps the most acceptable measure of air program progress, i.e., observed changes in the atmosphere consistent with expectations of emissions strategies. Accountability is the closest direct match to measurements in addressing agency goals as outlined in the Government Performance and Results Act of 1993 (GPRA), and applies to all programs (MACT, residual risk, area sources, mobile source rules, and local-scale projects).
- *Problem Identification:* Measurements are used to uncover a suspected air quality issue associated with a specific source or source group, or confirm that a problem does not exist. Given the numerous HAPs and variation in issues across the nation, this particular objective probably contributed to much of the historical toxics monitoring as well as the emerging local-scale project studies. Local-scale project studies are used to pinpoint a particular pollutant that may be present in only one city or even a part of a city. This type of project is usually very intensive, short in duration, and targets very specific compounds.
- *Science Support:* Routine network measurements often provide a backbone of basis measurements that more extensive research studies can utilize in the areas of model process development, exposure studies, and health effects. By themselves, data from the network should provide a basis for a wealth of long-term epidemiological studies associating adverse health impacts with observations, particularly where toxics measurements are grouped with multiple pollutants. In addition, given the current limited research efforts on methods development, the national air toxics program can also provide opportunities to test and advance measurement methodologies for air toxics.

Air toxics methods are generally classified into two groups: organic and inorganic. Organic refers to the class of compounds that contain carbon. Inorganic refers to the analyses of non-carbon elements and matrices. EPA created what is known as the Compendium (plural: compendia), which is a compilation of sampling and analytical methods brought into a larger set of volumes. Originally developed by the Office of Research and Development (ORD) in late 1990s, they have since been reviewed and revised, and new methods have been created. The Office of Air Quality Planning and Standards (OAQPS) now develops air toxics methods. All of these organic and inorganic methods are available on the EPA's Technology Transfer Network (ttn) websites:

- http://www.epa.gov/ttn/amtic/inorg.html
- http://www.epa.gov/ttn/amtic/airtox.html

Figure 8-6 is the front cover of the Compendium Methods for the Determination of Toxic Organic Compounds in Ambient Air. An additional Compendium, Determination of Inorganic Compounds in Ambient Air, is also available on the EPA's website. Before these methods could be added to the Compendium, they went through very thorough review by EPA and its stakeholders. Although these methods have their flaws, they are the backbone of the HAPs methods.



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EPA/625/R-96/010b
January 1999

Research and Development

EPA

Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air - Second Edition

Figure 8-6. Front cover of the TO Compendium.

One additional document, the Technical Assistance Document for the National Ambient Air Toxics Trends and Assessment Program (NATTS TAD) is also useful to operators and laboratory staff. This document describes the most current recommendations on the toxic organic (TO) and inorganic (IO) methods. It can be found at: http://www.epa.gov/ttn/amtic/airtox.html.

Description of the Methods

This section will describe the most widely utilized methods in the Compendia. Please note that these are guidance documents and describe the general procedures to obtain data. Many laboratories use these as their starting point and detail their modifications in their individual standard operating procedures.

The objective of the Compendia is for the EPA to document and standardize methods for measuring atmospheric pollutants of interest and publish them in standardized format, with each having been extensively reviewed by several technical experts having expertise in the methodology presented. Tables 8-1 and 8-2 illustrate how the TO and IO Compendia are organized.

Table 8-1. Toxic Organic Methods.

Method No.	Compounds
TO-1	VOCs
TO-2	VOCs
TO-3	VOCs
TO-4A	Pesticides and polychlorinated biphenyls
TO-5	Aldehyde and ketones
TO-6	Phosgene
TO-7	Amines
TO-8	Phenols
TO-9A	Dioxin/furans
TO-10A	Pesticides and polychlorinated biphenyls
TO-11A	Aldehydes and ketones
TO-12	Non-methane organic compounds
TO-13A	Polycyclic aromatic hydrocarbons
TO-14A	Nonpolar VOCs by flame ionization
TO-15A	Polar VOCs by mass spectroscopy
TO-16	VOCs by open path spectroscopy
TO-17	VOCs collection by diffusion tubes

Table 8-2. Toxic Inorganic Methods.

Method No.	Compounds/Technique
IO-1	Sampling of particle matter 10 microns or less
IO-2	Sampling of total suspended particles
IO-3	Chemical speciation of particle matter
IO-4	Determination of reactive acidic and basic gases
IO-5	Sampling and analysis of mercury

The remainder of this section will focus on the four methods that are used extensively throughout the air toxics networks. They are:

- **TO-11A:** Carbonyls (ketones and aldehydes) by dinitrophenylhydrazine coated cartridge and liquid chromatography,
- **TO-13A:** Polynuclear aromatic hydrocarbons by polyurethane foam sampler and gas chromatography/mass spectrometry (GCMS),
- **TO-15A:** Volatile organic compounds (VOCs) by canister and GCMS, and
- **IO-3.5:** Metals by high-volume sampler on quartz filter using ion coupled plasma with mass spectrometer (ICP/MS).

Compendium Method TO-11A

This method is applied to the determination of formaldehyde and other carbonyl compounds (aldehydes and ketones) in ambient air. EPA Compendium Method TO-11A utilizes a coated solid adsorbent for collection of carbonyl compounds from ambient air followed by high pressure liquid chromatography (HPLC) analysis with ultraviolet (UV) detection. Carbonyl compounds, especially low molecular weight aldehydes and ketones, have received increased attention in the regulatory community due in part to their effects on humans and animals. Exposure to formaldehyde and other specific aldehydes (acetaldehyde, acrolein, and crotonaldehyde), even short-term, has been proven to cause irritation of the eyes, skin, and mucous membranes of the upper respiratory tract. High concentrations of carbonyls, especially formaldehyde, can injure the lungs and may contribute to eye irritation and affect other organs of the body. Aldehydes may also cause injury to plants. Sources of carbonyl compounds in ambient air range from natural occurrences to secondary formation through atmospheric photochemical reactions.

In general, natural sources of carbonyls do not appear to be important contributors to air pollution. Aldehydes are commercially manufactured by various processes, including production of alkenes, dehydrogenation of alcohols, and addition reactions between aldehydes and other compounds. Formaldehyde and other aldehyde production in the United States has shown a substantial growth over the last several years due in part to use of these compounds in a wide variety of industries, such as the chemical, rubber, tanning, paper, perfume, and food industries. The major industrial use of carbonyl compounds is as an intermediate in the syntheses of organic compounds, including alcohols, carboxylic acids, dyes, and medicines.

A major source of carbonyl compounds in the atmosphere may be attributed to motor vehicle emissions. In particular, formaldehyde, the major carbonyl compound in automobile exhaust, accounts for 50 to 70% of the total carbonyl burden in the atmosphere. Furthermore, motor vehicles also emit reactive hydrocarbons that undergo photochemical oxidation to produce formaldehyde and other carbonyl compounds in the atmosphere.

To address the need for a measurement method that determines carbonyl compounds with the sensitivity required to perform health risk assessments (i.e., 10^{-6} risk level), a combination of wet chemistry and solid adsorbent methodology was developed. Activating or wetting the surface of an adsorbent with a chemical specific for reacting with carbonyl compounds allowed greater volumes of air to be sampled, thus enabling better sensitivity in the methodology. Various chemicals and adsorbent combinations have been utilized with various levels of success. The currently accepted technique is based on reacting airborne carbonyls with 2,4-dinitrophenylhydrazine (DNPH) coated on a silica gel adsorbent cartridge, followed by separation and analysis of the hydrazone derivative by HPLC with UV detection. The methodology used to accomplish carbonyl compounds measurements is EPA Compendium Method TO-11A (http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-11ar.pdf). EPA Compendium Method TO-11A provides sensitive and accurate measurements of carbonyl compounds and includes sample collection and analysis procedures. In this method, a cartridge containing a coated solid sorbent is used to capture the compounds of interest (see Figure 8-7). The sampling cartridge is extracted and the extract is analyzed using HPLC with UV detection.

Figure 8-7. Examples of DNPH cartridges.

Organic compounds that have the same HPLC retention time and significant absorbance at 360 nanometers (nm) (the absorption of the DNPH derivative of formaldehyde) will interfere. Such interferences can often be overcome by altering the chromatographic separation conditions (e.g., using alternative HPLC columns or mobile phase compositions). Ozone has been identified as an interferent in the measurement of carbonyl compounds when EPA Compendium Method TO-11A is used. To eliminate this interference, removal or scrubbing of O_3 from the sample airstream in the field is mandatory. Ozone at high concentrations has been shown to interfere negatively in the sampling process by reacting with both the DNPH and its carbonyl derivatives (hydrazones) on the cartridge. The extent of interference depends on the temporal variations of both the ozone and the carbonyl compounds and the duration of sampling. Significant negative interference from O_3 has been observed at concentrations of formaldehyde and ozone typical of clean ambient air. Because of these issues, it is recommended that the ozone interference should be removed before the ambient air sample stream reaches the coated cartridge.

Figure 8-8 illustrates a block diagram of a typical TO-11A sampler. Note that the air is drawn in through a manifold, then through a denuder. The denuder scrubber is constructed using a saturated solution of potassium iodide (KI) to selectively remove ozone from the sample air.

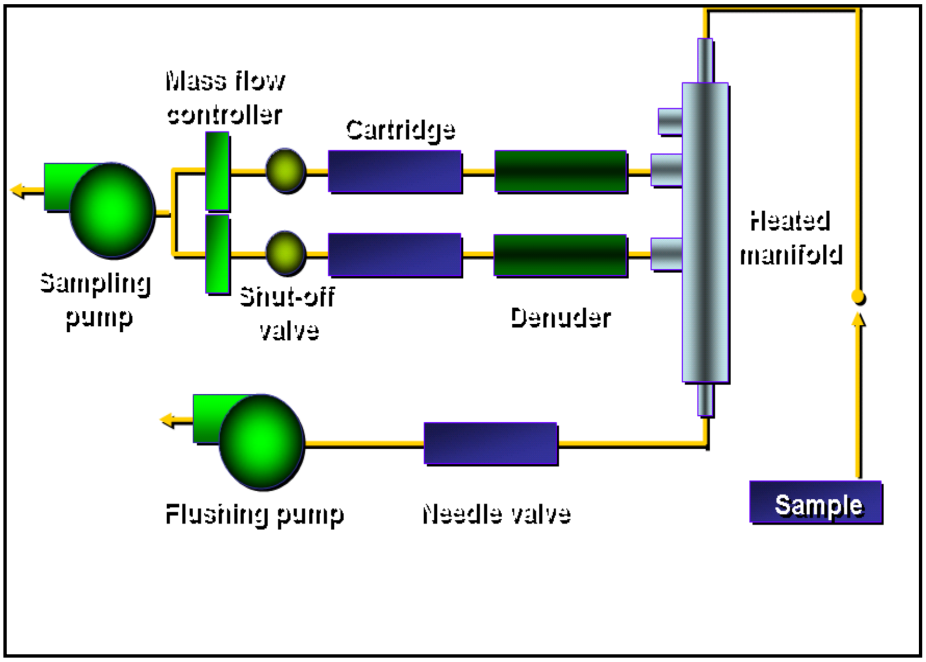

Figure 8-8. Diagram of a TO-11A sampler.

Compendium Method TO-13A

Method 13A is the method best suited for determining SVOCs in ambient air. SVOCs are the class of organic compounds that can be either gases or solids under ambient conditions. Compounds like naphthalene, anthracene, and benzoapyrene are examples of SVOCs.

Sample collection for quantitative determination of SVOCs is accomplished by pulling ambient air at a known and constant flow rate through a quartz fiber filter followed by a sampling cartridge with a polyurethane foam (PUF) plug sandwiched between an adsorbent material, XAD-2®. The sampler pulls ambient air through the filter/PUF/XAD-2® media for a 24-hour collection period. Figure 8-9 illustrates a block diagram of a PUF sampler.

The sampler should be located in an unobstructed area at least 2 meters from any obstacle to airflow. The inlet of the high-volume sampler must be positioned in the breathing zone, 4 to 10 feet above ground level. The exhaust hose should be stretched out in the downwind direction to prevent recycling of air into the sampling head.

The high-volume sampler is calibrated using a calibrated orifice transfer standard (i.e., high-volume sampler calibrator) in accordance with the specifications of EPA Compendium Method TO-13A. The individual orifice plates are placed in the sampling flow stream, and the differential pressure across the orifice plate is documented. Simultaneously, a corresponding Magnehelic® pressure reading is recorded. The differential pressure and the Magnehelic® readings are used to create a curve that establishes the flow characteristics of each individual sampler.

The prepared XAD-2® cartridge is placed and secured into the sampling head of the high-volume sampler. The quartz fiber filter is placed and secured onto the inlet of the high-volume sampler. The system is activated manually and the desired Magnehelic® reading is achieved by adjusting the ball valve located at the exit of the sampling head.

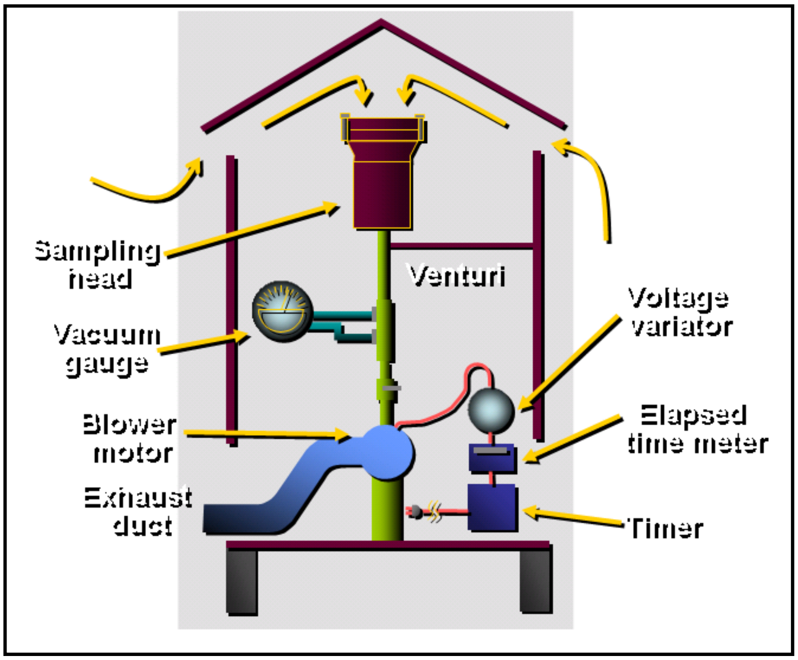

Figure 8-9. Block diagram of a PUF sampler.

Note that the Magnehelic® readings associated with use of a glass frit XAD-2® cartridge will be significantly lower than the readings typically achieved using polyurethane foam (PUF) cartridges because the glass frit material is more restrictive of flow. Readings in the range of 8 to 30 inches H_2O for glass frit XAD-2® cartridges are not unusual. Please see Figure 8-10 for a diagram of the PUF/XAD-2® sandwich.

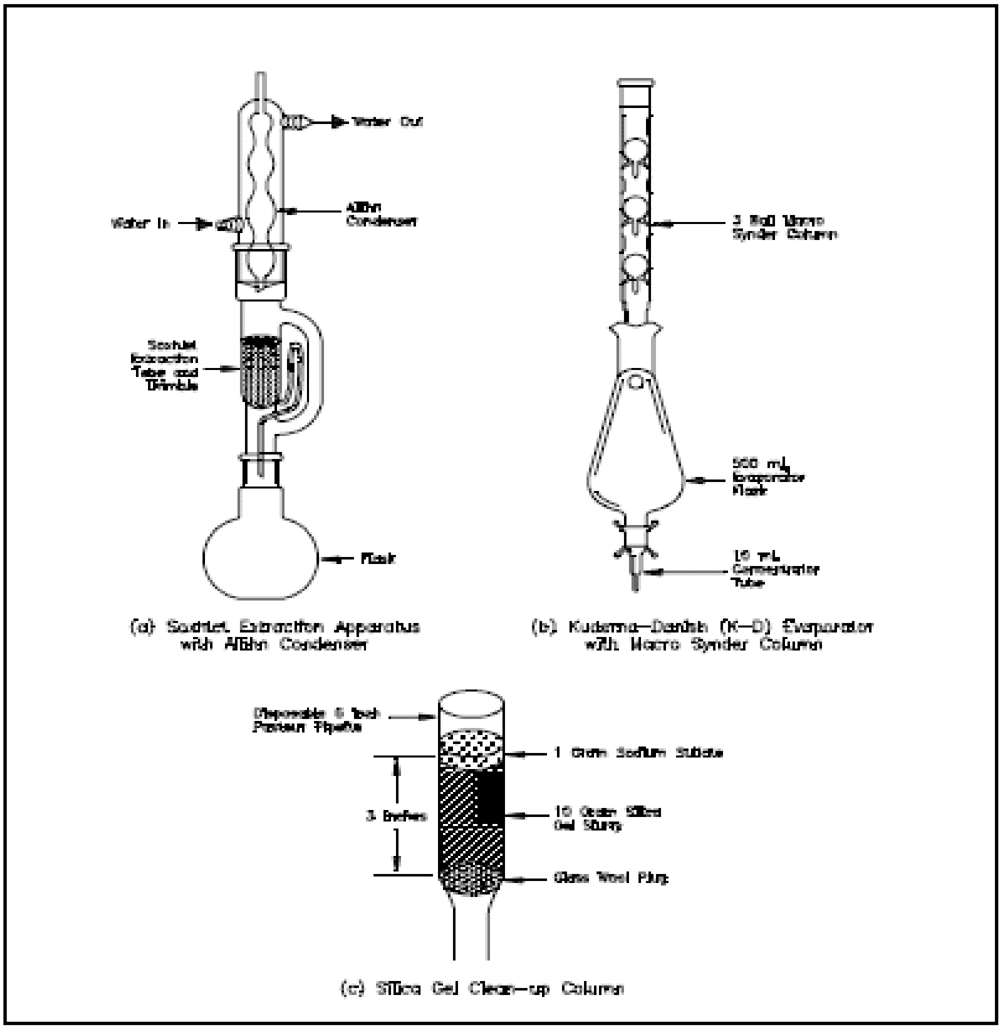

Figure 8-10. Diagrams of the Soxlet, K-D, and PUF/XAD-2® sandwich.

The analysis is performed by extracting the filters, XAD-2®, and PUF plug using a Soxhlet flask with an appropriate solvent. The extract is concentrated by a Kuderna-Danish (K-D) evaporator, followed by silica gel cleanup using column chromatography to remove potential interferences prior to analysis by GC/MS. The eluent is further concentrated by K-D evaporation, then analyzed by GC/MS. The analytical system is verified to be operating properly and is calibrated with five concentration calibration solutions.

Compendium Method TO-15A

Compendium Method T0-15A is the one of EPA's recommended methods for determining VOCs. Examples of VOCs that are characterized well by this method are benzene, vinyl chloride, and carbon tetrachloride.

The ambient air is drawn into a specially prepared stainless steel canister. A sample of air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling, and into the pre-evacuated and passivated canister. After the air sample is collected, the canister valve is closed and then transported to the laboratory. Figure 8-11 is a picture of a passivated canister that is widely used today.

Figure 8-11. Passivated canister.

These canisters can be reused many times over many years. They must be cleaned using clean, purified, humidified air. This process is outlined in the method.

To analyze the sample, a known volume is directed from the canister through a mass flow controller to a solid multisorbent concentrator. As a whole air sample, ambient humidity (i.e., water vapor) levels will be present. This water vapor can complicate the analysis. A portion of the water vapor will pass through the concentrator during sample concentration. The water vapor content of the concentrated sample can be reduced by dry purging the concentrator with dry helium.

Figure 8-12 illustrates a block diagram of the flow path of the VOCs. After the concentration and drying steps are completed, the VOCs are thermally desorbed, entrained in a carrier gas stream, and then focused into a small volume by trapping on a reduced temperature trap or small volume multisorbent trap. The VOCs are then released from the trap by thermal desorption and swept by the carrier gas onto a gas chromatographic column for separation.

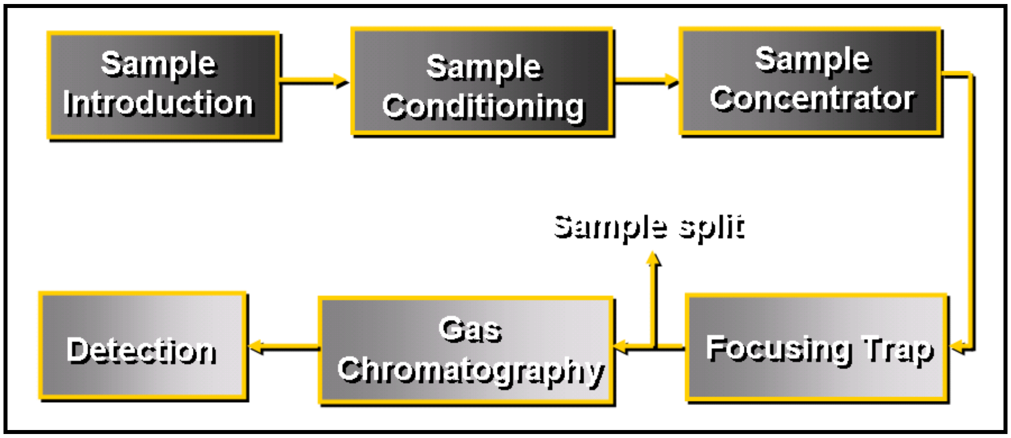

Figure 8-12. Flow diagram of the TO-15A method.

The analytical strategy involves using a high-resolution gas chromatograph (HRGC) coupled to a mass spectrometer (MS) operated by selective ion monitoring (SIM) mode. The fragmentation pattern from interaction of individual molecules with the MS ionization source (electron beam) is compared with stored spectra taken under similar conditions in order to calibrate for and identify the compounds. For any given compound, the intensity of the given fragment is compared with the system response to the given fragment for known amounts of the compound to establish the compound concentration that exists in the sample.

Canisters should be manufactured using high-quality welding and cleaning techniques, and new or reconditioned canisters should be filled with humidified zero air and then analyzed after 24 hours to evaluate cleanliness. Although the 24-hour period is not a method requirement, new and reconditioned canisters have a higher potential for contamination due to the manufacturing processes, and it is therefore prudent to allow the humidified zero air to remain in the canister for a longer period to ensure that contaminants are desorbed from active sites. The cleaning apparatus, sampling system, and analytical system should be assembled from clean, high-quality components, and each system should be demonstrated to be free of contamination.

Compendium Method IO-3.5

EPA Compendium Method IO-3.5 is the measurement method used for sampling and analytical procedures for the measurement of metals in ambient air. Representative compounds would be arsenic, lead, or cadmium. The method involves collection on total suspended particulate (TSP) or particulate material $\leq$ 10 micron (PM_{10}) filters and detection by inductively coupled plasma/mass spectrometry (ICP/MS). ICP/MS uses an argon plasma torch to generate elemental ions for separation and identification by mass spectrometry. This analysis technique allows many more than 60 elements to be quantitatively determined simultaneously, and the isotopes of an element can also be determined.

Figure 8-13 illustrates two types of high-volume samplers: TSP and PM_{10} samplers. Ambient air is pulled through filter media using a high-volume sampler. The particulate phase sample is collected on the filter, and the filter is digested yielding the sample material in solution. Sample material in solution is introduced by pneumatic nebulization into a radio frequency plasma where energy transfer processes cause desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially-pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer having a minimum resolution capability of 1 amu peak width at 5% peak height. The ions transmitted through the quadrupole are registered by a continuous dynode electron multiplier, and the ion information is processed by a data-handling system.

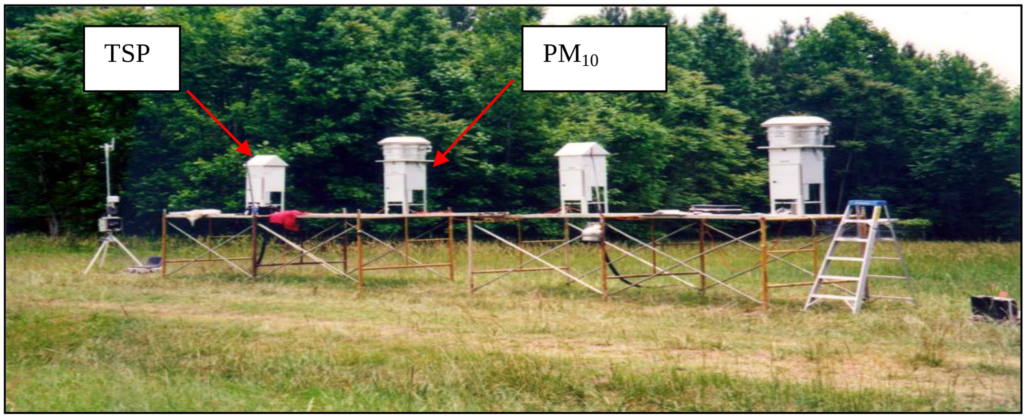

Figure 8-13. High-volume TSP and PM_{10} samplers.

Sample collection for quantitative determination of metal species is accomplished by pulling ambient air at a known and constant flow rate through a filter over a 24-hour collection period.

The glass fiber filter is 8 in. x 10 in. and is constructed of spectro-quality-grade glass fiber material with a pH of approximately 7.5. The filters must have a collection efficiency of 99% for particles of 0.3 µm in diameter or larger. Each filter must have a unique ID number that is a permanent part of the filter.

If the sampler is located on a roof or other structure, there must be a minimum of a 2-meter separation from walls, parapets, penthouses, etc. No furnace or incineration flues should be nearby. This separation distance from flues is dependent on the height of the flues, type of waste or fuel burned, and quality of fuel (ash content). In the case of emissions from a chimney resulting from natural gas combustion, the sampler should be placed at least 5 m from the chimney as a precautionary measure. On the other hand, if fuel oil, coal, or solid waste is burned and the stack is sufficiently short so that the plume could reasonably be expected to impact on the sampler intake a significant part of the time, other buildings/locations in the area that are free from these types of sources should be considered for sampling. Trees provide surfaces for particulate deposition and also restrict airflow. Therefore, the sampler should be placed at least 20 m from the drip line and must be 10 m from the drip line when the tree(s) acts as an obstruction. The sampler must also be located away from obstacles such as buildings, so that the distance between obstacles and the sampler is at least twice the height that the obstacle protrudes above the sampler, except for street canyon sites. Sampling stations that are located closer to obstacles than this criterion allows should not be classified as neighborhood, urban, or regional scale, since the measurements from such a station would closely represent middle-scale stations. Additional information for siting samplers is provided in 40 CFR Part 58, Appendix E.

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