U.S. ENVIRONMENTAL PROTECTION AGENCY

ANALYTICAL METHODS FOR AIR QUALITY STANDARDS

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AVAILABILITY

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Chapter 1

Introduction to Ambient Air Monitoring

The Environmental Protection Agency (EPA), under the authority of the Clean Air Act, has established National Ambient Air Quality Standards (NAAQS) for sulfur dioxide, particulate matter (PM_{10} and $PM_{2.5}$), carbon monoxide, ozone, nitrogen dioxide, and lead. These standards, contained in Title 40 Part 50 of the *Code of Federal Regulations* (CFR), are of two types: *primary standards* and *secondary standards*. As stated in Section 109 of the Clean Air Act, primary standards are those, "the attainment and maintenance of which are requisite to protect the public health." The section further defines a secondary ambient air quality standard as, "a level of air quality attainment and maintenance of which is requisite to protect the public welfare from any known or anticipated adverse effects associated with the presence of such air pollutants in the ambient air." In other words, primary standards are those promulgated to protect human health; secondary standards are for the protection of the general welfare (e.g., protection of plants, animals, materials, visibility, etc.). In addition, Section 109 of the Act requires the EPA to evaluate, at 5-year intervals, the criteria for which standards have been promulgated and to issue any new standards as may be appropriate.

These primary and secondary ambient air quality standards must be achieved throughout the United States and its possessions. In order to meet the standards, states are required to develop and implement air pollution control strategies through the mechanism of State Implementation Plans (SIPs). The implementation plans may contain control strategies such as industrial and urban zoning, the development or expansion of mass transit systems and vehicle inspection and maintenance programs, and the establishment of stationary source emissions standards for specific industrial categories. Ambient air monitoring plays a vital role in the development and evaluation of these control strategies. During the development phase, air quality data is used to determine if an area is attaining or not attaining the air quality standards. This determination is critical for the proper designing of control strategies for the area in question because attainment areas usually require less stringent control measures than nonattainment areas. Furthermore, air quality data may be used to generate or validate computer models of air pollution dispersion which are then used in the development of control strategies. After the implementation plans containing their various control strategies have been put into force, further ambient air quality monitoring is required in both attainment and nonattaiment areas. For areas that have achieved attainment, further monitoring is necessary to assure that attainment is maintained. Additional monitoring is required in nonattainment areas for evaluating progress toward reaching attainment.

In addition to the requirement that the primary and secondary NAAQS be achieved and maintained throughout the country, the Clean Air Act also stipulates that no significant deterioration of existing air quality will be allowed in any portion of any state. In order to comply with this provision, it is necessary to determine the impact on the existing air quality of an area by a planned new emissions source. The estimated emissions contributed by the new source must be compared to the existing air quality to ascertain whether the new source would significantly deteriorate the present air quality. Ambient air quality monitoring data is used to establish the preexisting air quality of the area in question.

In conjunction with the NAAQS, EPA has established detailed analytical methods for monitoring these pollutants. These methods, termed *reference methods,* are contained in Appendices A through L of 40 CFR 50 (Appendices A through L are also provided in Appendix 1 of this manual). Reference method is defined as “a method of sampling and analyzing the ambient air for an air pollutant that is specified as a reference method in an Appendix of 40 CFR Part 50, or a method that has been designated as a reference method in accordance with 40 CFR Part 53." (40 CFR Part 53 is included in Appendix 2 of this manual.) A summary of the applicable requirements for reference and equivalent methods for the monitoring of criteria pollutants are provided in Table 1-1.

TABLE 1-1. Summary of Applicable Requirements for Reference and Equivalent Methods for Air Monitoring of Criteria Pollutants (Reproduced from Table A-1 to Subpart A of 40 CFR Part 53).

Pollutant	Reference or Equivalent	Manual or Automated	Applicable Part 50 Appendix	Applicable Subparts of 40 CFR Part 53					
				A	B	C	D	E	F
SO_2	Reference	Manual	A						
	Equivalent	Manual		✓		✓			
		Automated		✓	✓	✓			
CO	Reference	Automated	C	✓	✓				
	Equivalent	Manual		✓		✓			
		Automated		✓	✓	✓			
O_3	Reference	Automated	D	✓	✓				
	Equivalent	Manual		✓		✓			
		Automated		✓	✓	✓			
NO_2	Reference	Automated	F	✓	✓				
	Equivalent	Manual		✓		✓			
		Automated		✓	✓	✓			
Pb	Reference	Manual	G						
	Equivalent	Manual		✓		✓			
PM_{10}	Reference	Manual	J	✓			✓		
	Equivalent	Manual		✓		✓	✓		
		Automated		✓		✓	✓		
$PM_{2.5}$	Reference	Manual	L	✓				✓	
	Equivalent Class I	Manual	L	✓		✓		✓	
	Equivalent Class II	Manual	L[1]	✓		✓[2]		✓	✓[1,2]

	Equivalent Class III	Automated	L[1]	✓		✓		✓[1]	✓[1]
$PM_{10-2.5}$	Reference	Manual	O[2]	✓				✓	
	Equivalent Class I	Manual	O[2]	✓				✓	
	Equivalent Class II	Manual	O[2]	✓		✓[2]		✓[1]	✓[1,2]
	Equivalent Class III	Automated	L[1], O[1,2]	✓		✓		✓[1]	✓[1]

[1] Some requirements may apply, based on the nature of each particular candidate method, as determined by the Administrator.
[2] Alternative Class III requirements may be substituted.

A reference method may be either manual or automated. The *manual reference methods* are detailed analytical procedures, with specifications on all important parameters. The pararosaniline method for SO_2 analysis is an example of a manual method, as are the reference methods for PM_{10} and $PM_{2.5}$. *Automated reference methods* depend on specified measurement principles (MP) and calibration procedures (CP). An automated reference method consists of a measurement principle which has been specified as reference by EPA, as well as, an EPA designated reference calibration procedure. Thus, for an automated reference method, any instrument using the reference measurement principle and calibrated by the reference calibration procedure can be designated as a separate reference method. This can be explained using the example of the reference measurement principle and calibration procedure for ozone determination -- chemiluminescence with ethylene and ultraviolet (UV) photometry, respectively. Several manufacturers make ozone analyzers which differ in various aspects, yet they all use the same chemiluminescence process and conform to EPA's specifications. Each manufacturer's instrument is considered a reference method, if it is designated as a reference method per 40 CFR Part 53, meets the performance specifications in Table 1-2, and is calibrated using the UV photometry calibration procedure.

Table 1-2. Performance specifications for automated (gaseous) methods (Reproduced from Table B-1 of 40 CR Part 53 Subpart B).

Performance parameter	Units[1]	Sulfur dioxide	Ozone	Carbon monoxide	Nitrogen dioxide	Definitions & test procedures
Range	ppm	0–0.5	0–0.5	0–50	0–0.5	Sec. 53.23(a)
Noise	ppm	.005	.005	.50	.005	Sec. 53.23(b)
Lower detectable limit	ppm	.01	.01	1.0	.01	Sec. 53.23(c)
Interference equivalent						Sec. 53.23(d)
Each interferant	ppm	±.02	±.02	±1.0	±0.02	
Total interferant	ppm	.06	.06	1.5	.04	
Zero drift, 12 & 24 hour	ppm	±.02	±.02	±1.0	±.02	Sec. 52.23(e)
Span drift, 24 hour						Sec. 52.23(e)
20 % of upper range limit	%	±20.0	±20.0	±10.0	±20.0	
80 % of upper range limit	%	±5.0	±5.0	±2.5	±5.0	
Lag time	mins.	20	20	10	20	Sec. 52.23(e)
Rise time	mins.	15	15	5	15	Sec. 52.23(e)
Fall time	mins.	15	15	5	15	Sec. 52.23(e)

Precision						Sec. 52.23(e)
20 % of upper range limit	ppm	.01	.01	.5	.02	
80 % of upper range limit	ppm	.015	.01	.5	.03	

[1] To convert from ppm to ug/m^{3}at 25 ^{o}C and 760 mm Hg. Multiply by M/0.02447, where M is the molecular weight of the gas.

Some methods of air pollution analysis are designated *equivalent methods* by EPA. An equivalent method is "a method of sampling the ambient air for an air pollutant that has designated as an method in accordance with 40 CFR Part 53" as stated in 40 CFR Part 50.1. Two types of methods may be considered for equivalent method status: *manual methods and automated methods.* For a manual method to be designated as an equivalent method, it must demonstrate a consistent relationship to the reference method used to measure pollutant concentrations in a real atmosphere. In other words, the reference method and candidate manual method sample the same air in a "field" monitoring situation and the manual method's results must match (with some allowances) the results of the reference method. For automated methods to attain equivalent method status, they must be able to meet or exceed the performance standards specified by EPA in 40 CFR 53B. These specifications are given in Table 1-2. In addition, the candidate method must meet the consistent relationship requirements of Table 1-3. A current list of all reference and equivalent methods is maintained and updated by EPA whenever a new method is designated. This list can be found on the *AMTIC Bulletin Board* at http://www.epa.gov/ttn/amtic.

Table 1-3. Test concentration ranges, number of measurements required, and maximum discrepancy specification (Reproduced from Table C-1 to Subpart C of Part 53).

Pollutant	Concentration range (parts per million)	Simultaneous measurements required				Maximum discrepancy specification (parts per million)
		1-hr		24-hr		
		First set	Second set	First set	Second set	
Ozone	Low 0.06 to 0.10..........	5	6	....	....	0.02
	Med 0.15 to 0.2...........	5	6	....	....	0.03
	High 0.35 to 0.45.........	4	6	....	....	0.04
	Total	14	18	....	....	....
Carbon monoxide	Low 7 to 11.................	5	6	....	....	1.5
	Med 20 to 30..............	5	6	....	....	2.0
	High 35 to 45..............	4	6	....	....	3.0
	Total	14	18	....	....	....
Sulfur dioxide	Low 0.02 to 0.05..........	....	....	3	3	0.02
	Med 0.10 to 0.1...........	....	....	2	3	0.03
	High 0.30 to 0.50.........	7	8	2	2	0.04
	Total	7	8	7	8	....
Nitrogen dioxide	Low 0.02 to 0.08..........	....	....	3	3	0.02
	Med 0.10 to 0.20..........	....	....	2	3	0.03
	High 0.25 to 0.35.........	....	....	2	2	0.03
	Total............................	....	....	7	8	....

All formal sampler design and performance requirements and the operational requirements applicable to reference methods for PM_{10} and $PM_{2.5}$ are specified in Appendix J and L of 40 CFR Part 50, respectively. The requirements, for $PM_{2.5}$ federal reference method (FRM) samplers, are quite specific and include explicit design specifications for the type of sampler, the type of filter, the sample flow rate, and the construction of the sample collecting components. However, various designs for the flow-rate control system, the filter holder, the operator interface controls, and the exterior housing are possible. Hence, various reference method samplers from different manufacturers may vary considerably in appearance and operation. Also, a reference method may have a single filter capability (single sample sampler) or a multiple filter capability (sequential sample sampler), provided no deviations are necessary in the design and construction of the sample collection components specified in the reference method regulation. A $PM_{2.5}$ method is not a reference method until it has been demonstrated to meet all the reference method regulatory requirements and has been officially designated by EPA as a reference method for $PM_{2.5}$.

Equivalent methods for $PM_{2.5}$ have much wider latitude in their design, configuration, and operating principle than reference methods. These methods are not required to be based on filter collection of $PM_{2.5}$; therefore, continuous or semi-continuous 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 reference methods, but they must demonstrate both *comparability* to reference method measurements and similar $PM_{2.5}$ *measurement precision*. The requirements that some (but not all) candidate methods must meet to be designated by EPA as equivalent methods are specified in 40 CFR Part 53. To minimize the difficulty of meeting equivalent method designation requirements, three classes of equivalent methods have been established in the 40 CFR Part 53 regulations based on a candidate method's extent of deviation from the reference method requirements. All three classes of equivalent methods are acceptable for SLAMS or SLAMS-related $PM_{2.5}$ monitoring, but not all types of equivalent methods may be equally suited to various $PM_{2.5}$ monitoring requirements or applications.

In addition to the regulations to reference and equivalent methods described in 40 CFR 50 and 53, 40 CFR 58 contains requirements for reference and equivalent methods used at State Local Air Monitoring Stations (SLAMS) and at Prevention of Significant (PSD) monitoring stations. Appendices A and B of 40 CFR 58 describe quality assurance requirements for SLAMS monitoring networks and PSD monitoring networks, respectively. Appendix C of 40 CFR 58 specifies the use of reference and equivalent methods in SLAMS and PSD monitoring networks. 40 CFR 58 Appendix E specifies probe materials (i.e., FEP Teflon®, borosilicate glass, or their equivalent) and pollutant-sample resident time in probes (i.e., less than 20 seconds) for SO_2, NO_2, and O_3 monitors of SLAMS monitoring networks.

Traditionally, NAAQS pollutants have been monitored because of their deleterious human health effects and due to their ubiquitous distribution nationwide. National and site-specific trends of the NAAQS can be found at http://www.epa.gov/oar/airtrends/. On average, substantial reductions have been achieved for each of the NAAQS since 1980. However, ozone and particulate matter remain as pollutants of special concern, particularly, in high population areas.

In addition to NAAQS monitoring, recent efforts have expanded ambient monitoring for other harmful pollutants. Specifically, the EPA Air Toxics program works with state, local, and tribal governments in order to quantify and reduce emissions of approximately 188 hazardous pollutants found in ambient air, more commonly known as “air toxics”. These “air toxics” are pollutants that are known or suspected to cause cancer or other serious health effects, such as reproductive effects or birth defects, or adverse environmental effects. Additional information, as provided by EPA, on the air toxics program can be found at http://www.epa.gov/oar/toxicair/newtoxics.html.

Dramatic and mostly positive changes in air quality have been observed over the last two decades, despite increasing population, vehicle usage, and productivity. Most criteria pollutant measurements read well below national standards. In response to these changes and an increased concern over air toxics a new National Ambient Air Monitoring Strategy (NAAMS) was adopted in 2006. Under the recently adopted NAAMS, monitoring objects have evolved to allow for more flexibility and emphasis on monitoring for those traditional pollutants which continue to persistent (i.e., particulate matter, ozone, and constituents of acid deposition) and an expansion and redirection of existing efforts and development of new capacity to monitor for air toxics.

In order to accurately quantify constituents in the ambient air it is necessary to measure sample gas parameters, such as: temperature, pressure, humidity, gas composition, and flow rate. The importance of these parameters and how they are accounted for will be discussed in detail in Chapter 2 of this Manual.

The topics discussed in subsequent chapters include a detailed discussion of the measurement principle and calibration procedures for each of the gaseous *criteria pollutants* (i.e., carbon monoxide, sulfur dioxide, ozone, and nitrogen dioxide) including special considerations for monitoring for precursor gas concentration levels, procedures for the generation of test atmospheres needed to calibrate ambient air monitors, and the framework of the recently adopted National Ambient Air Monitoring Strategy (NAAMS).

In addition to the discussion presented in this manual, hands-on laboratory exercises have been developed to provide the students a realistic experience in the operation and calibration of ambient monitors. These exercises are contained in the accompanying Laboratory Exercise Manual.

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Chapter 2

Basic Gas Properties and Mathematical Manipulations

This chapter identifies the basic gas properties and mathematical manipulations.

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 be able to convert from one system to the other, the following equations can be used:

(Eq. 2-1)
$$°F = 1.8°C + 32$$

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

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) ${}^\circ R = {}^\circ F + 459.67$

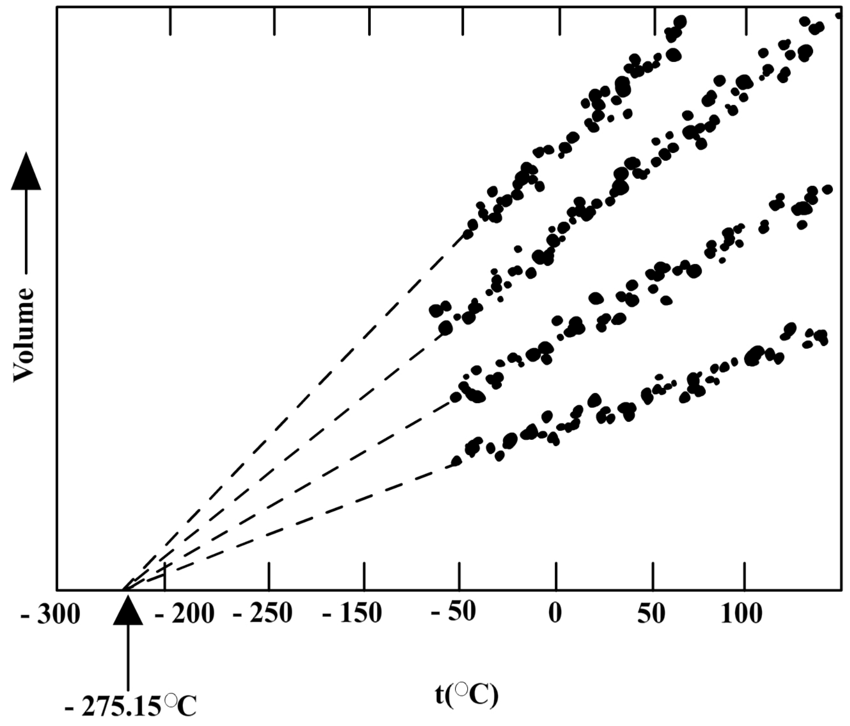

Figure 2-1(a). Temperature relationships.

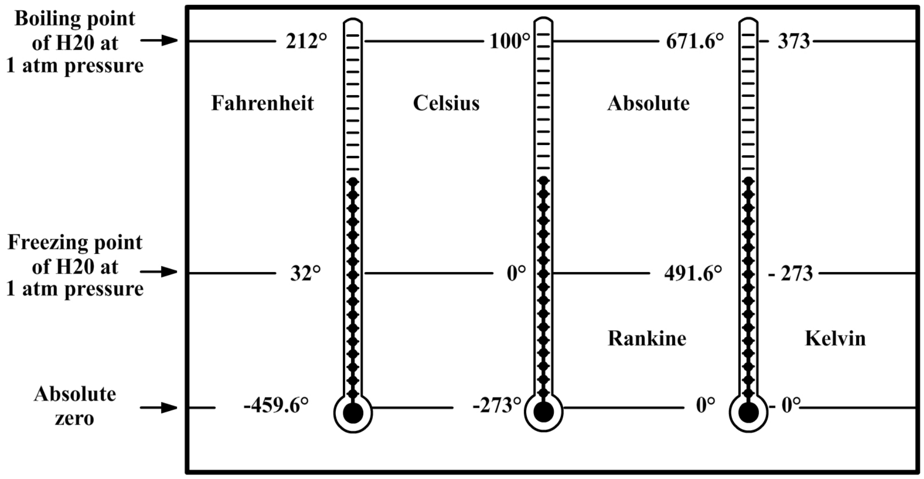

Figure 2-1(b). Relationships of the absolute temperature systems.

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.

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
$\mathrm{gm}_f / \mathrm{cm}^2$	$\mathrm{lb}_f / \mathrm{in.}^2$ (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.

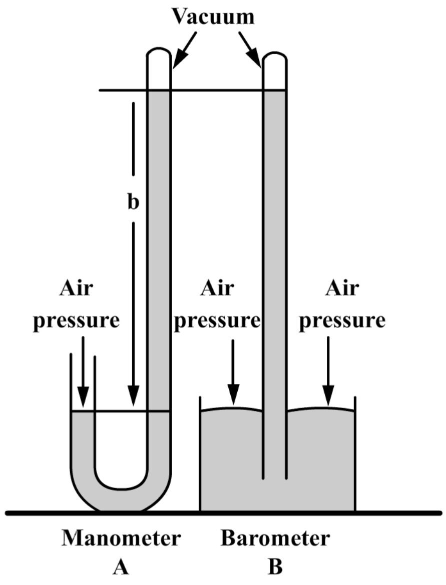

Figure 2-2. The manometer and mercurial barometer.

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.

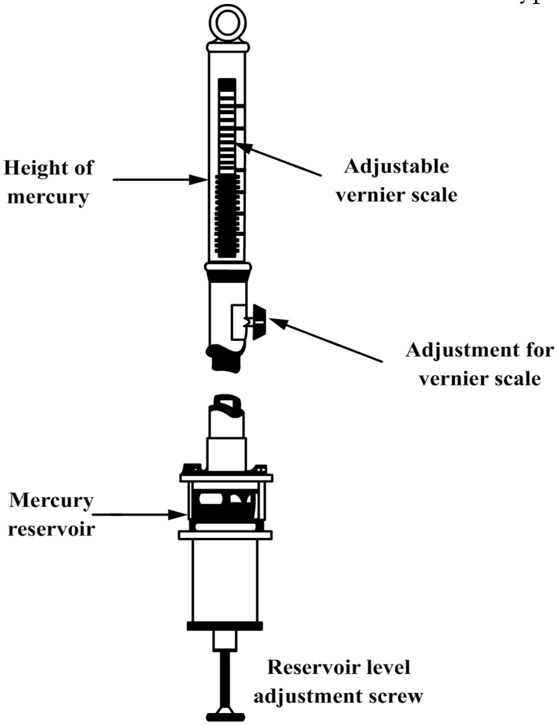

Figure 2-3. Fortin barometer.

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.

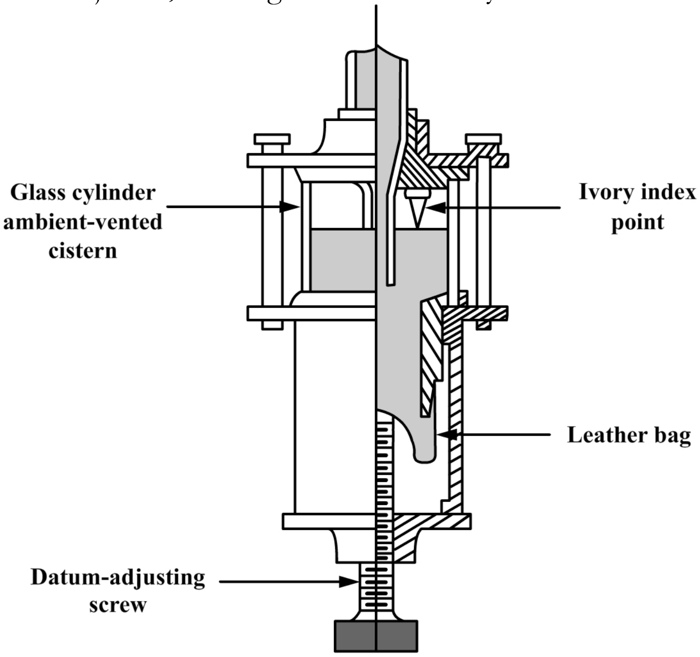

Figure 2-4. Blow-up of Fortin barometer.

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.

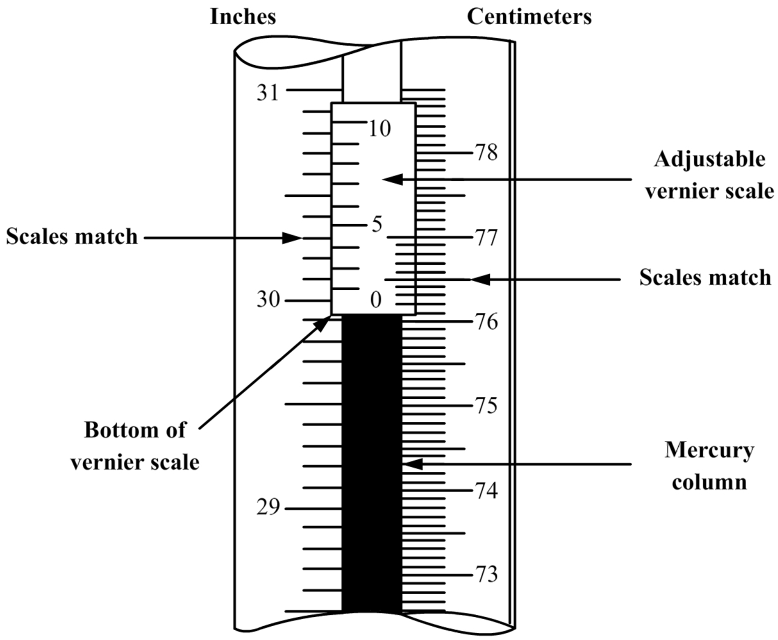

Figure 2-5. Blow-up of vernier scale.

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.

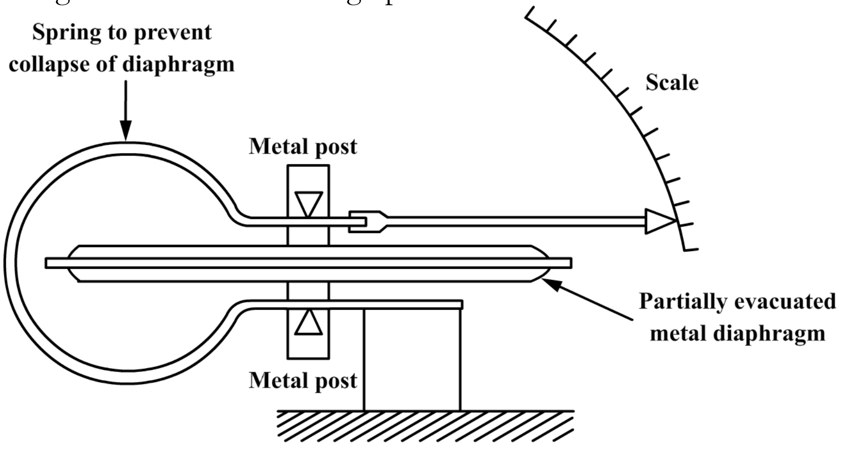

Figure 2-6. Aneroid barometer.

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 use of the principles of conductivity and capacitance to measure pressure. A *strain gauge* the use of 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 would be that there are 50 different technologies and hundreds of companies making pressure sensors.

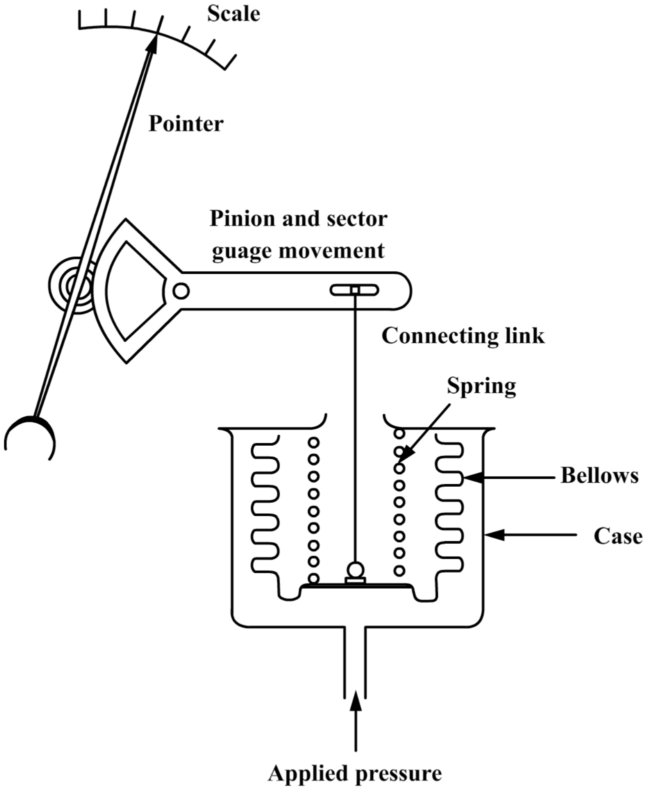

Figure 2-7. Mechanical pressure transducer.

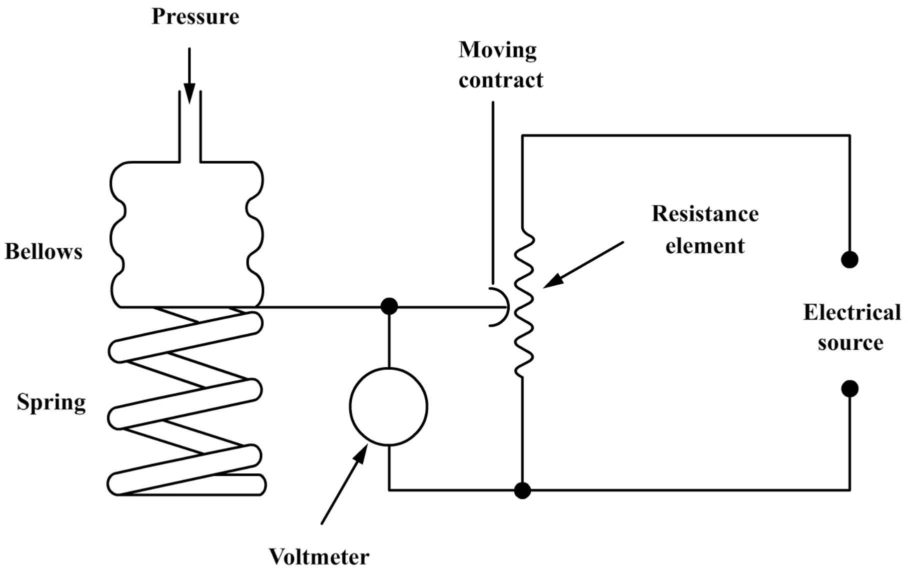

Figure 2-8. Electrical pressure trasducer.

Gauge Pressure

Gauges indicate the pressure of the system of which they are a part 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, 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. 2-3)

$$P = P_b + \rho_g$$

Where: P = *absolute pressure*
P_b = *atmospheric pressure*
ρ_g = *gauge pressure*

Note: P, P_b, and ρ_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. It is convention to denote a gauge pressure 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, hence, is expressed as a positive value. Gauge reading 2 is below the prevailing atmospheric pressure and, therefore, is expressed as a negative value. Gauge reading 3 has both sides open to the atmosphere; hence, the gauge pressure is zero.

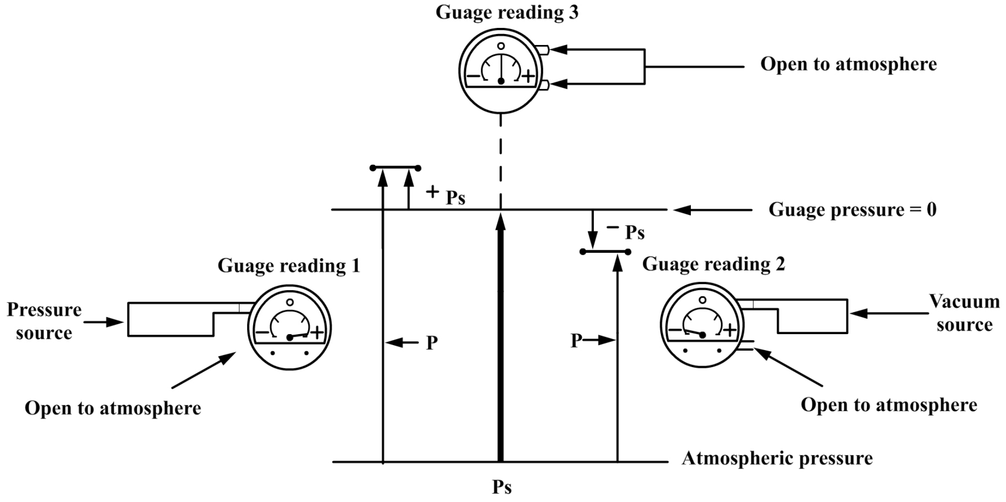

Figure 2-9. Absolute-atmospheric-guage pressure relationship.

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:

$$P = P_b + p_g = 14.2 + 2000$$

$$P = 2014.2 \, psia.$$

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=O (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. 2-4)
$$p = \rho_f h\left(\frac{g}{g_c}\right)$$

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*
$\sum p_i$ = $p_1 + p_2 + \ldots + p_{19}$

($\sum$: means "sum of")

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.:

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

Where: α *= 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.,:*

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

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' Law are satisfied in the following equation:

(Eq. 2-5) $$PV = n\mathrm{R}T$$

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 substances 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:

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

Where the units are:
$V(\ell)$
$m(\mathrm{g})$
$M(\mathrm{g/g}\text{-}mole)$
$T(\mathrm{K})$
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 ºC) 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 = $62.4\,(\ell)(\mathrm{mmHg})(\mathrm{g}\text{-}mole)^{-1}(K)^{-1}$
T = 273 K
V = V *(molar volume)*

then:

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

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 24.46ℓ. The volume per *mole* constant for any gas at a given pressure and temperature is called the *molar volume* and is symbolized by $\overline{V}$.

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. 2-6)

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

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

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

$$\rho = \frac{M\,\dfrac{298}{T}\,\dfrac{P}{760}}{24.46}$$

, corrected to standard temperature and pressure conditions

Where: ρ = *gas density* (g/ℓ)
M = *molecular weight* ($\text{g}/\text{g - }mole$)
24.46 = *molar volume* ($\ell/\text{g - }mole$)
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. 2-7)

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

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

$$V2 = (V1)(0.39)\left(\frac{P_1}{T_1}\right)$$

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. 2-8)

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

Where:

g_c = *dimensional constant*
T = *unit shearing stress between adjacent layers of fluid*
$\frac{dv}{dy}$ = *velocity gradient*

μ = *proportionality constant (viscosity)*

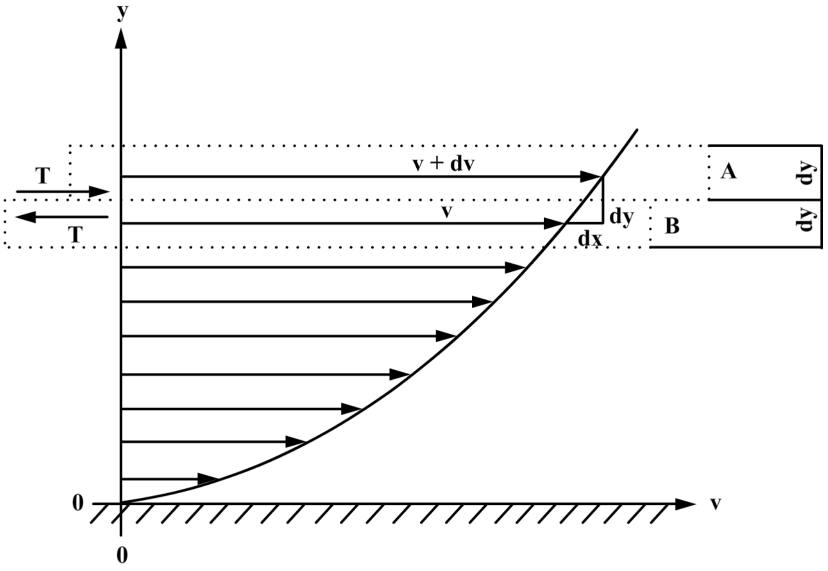

Figure 2-10. Velocity gradient.

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 2-8, 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. 2-9)

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

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 2-8 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 is increased when the temperature increases.

Determination of Viscosity of Gases

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

(Eq. 2-10)

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

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

μ° = *viscosity at* $0^\circ C$ *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.

Reynold's Number

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:
(1-20)

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

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:

(1-21)

$$\mathrm{Re} = \frac{Dv\rho}{\mu}$$

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, describes the particle velocity relative to the gas stream:

(1-22)

$$\mathrm{Re}_p = \frac{D_p v_p \rho}{\mu}$$

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 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 um, 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 capture will be altered as well. The concept 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*.

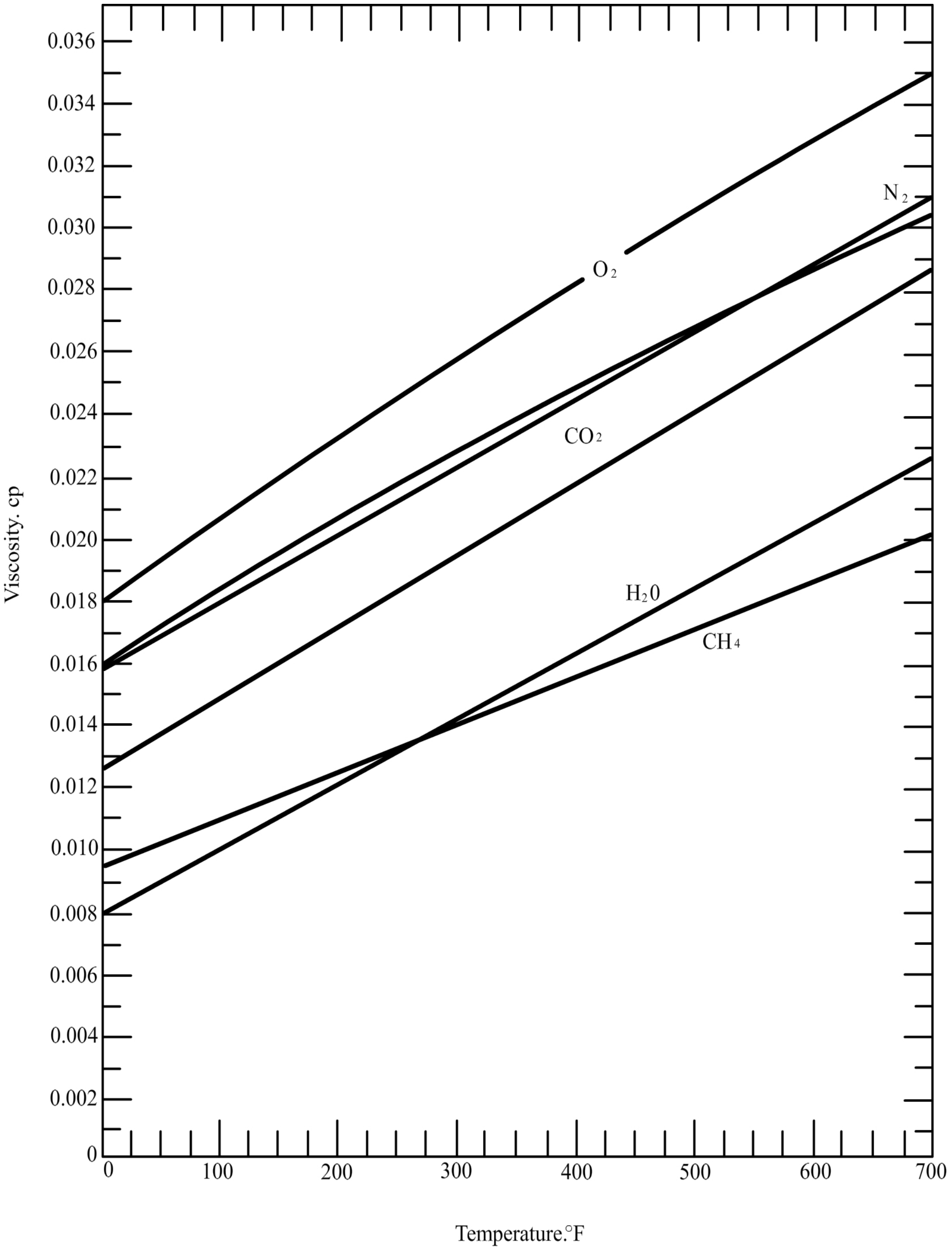

Figure 2-12. Viscosity nomograph of various gases at 1 atmosphere.

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

$$\mathrm{P} = \mathrm{P_b} + \mathrm{p_g}$$

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

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

$$1\ std\ atm = 29.92\ \mathrm{in.\ Hg}$$

$$= 760\ \mathrm{mm\ Hg}$$

Where: P = *absolute pressure*
p = *pressure*
ρ = *density*
h = *pressure-head or height*
g = *gravitational acceleration*
g_c = *dimensional constant*
<u>*Subscripts*</u>
g = *gauge*
f = *fluid*
b = *barometric or atmospheric*

Ideal Gas Law

$$PV = nRT$$

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

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

$$= \frac{62.4\,(\mathrm{liters})(\mathrm{mm\ Hg})}{(\mathrm{g}\text{ - }mole)(\mathrm{K})}$$

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

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

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

Viscosity, μ

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

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

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

Reynold's Number

$$N_{\mathrm{Re}} = \frac{Lv\rho}{\mu} = \frac{inertial\ force}{viscous\ force}$$

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*
N_{Re} = *Reynold's Number*

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 carry-overs 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	$\mu g/m^3$ (std)	10 to 5000 $\mu g/m^3$ as TSP 30 to 140 $\mu g/m^3$ as PM10 [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 ug/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 millimeter 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
Particle count in sedimentation devices (horizontal and vertical)	– –	Number of particles/cm^2/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	– –

Note 1: Based on National Trends data for PM10 & PM2.5.

Conversion Problems

Sample Gas Problem

Discussion:

The expression parts per million is without dimensions, i.e., no units of weight or volume are specifically designed. 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 $^{\mu\ell}/\ell$. 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)

$$\frac{2.5\mu\ell}{\ell}\times\frac{1\mu\text{mole}*}{24.46\mu\ell}\times\frac{64.1\mu\text{g}}{\mu\text{mole}}\times\frac{1000\ell}{\text{m}^3}=6.5\times10^3\,\frac{\mu\text{g}}{\text{m}^3}\text{ at STP}$$

(b)

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

$$\frac{2.5\mu\ell}{\ell}\times\frac{1\mu\text{mole}}{25.73\mu\ell}\times\frac{64.1\mu\text{g}}{\mu\text{mole}}\times\frac{1000\ell}{\text{m}^3}=6.2\times10^3\,\frac{\mu\text{g}}{\text{m}^3}\text{ at 37°C, 752 mm Hg}$$

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

*Since, at STP, 1 mole of a gas occupies 24.46 liters, 1 μmole = 24.46 $\mu\ell$.

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 A3 of this manual.

Significant Figures and Rounding Off

In most cases, rather than using paper and pencil, you will be performing math calculations using a handheld calculator, a personal computer, or a mainframe computer. However, whether you use an electronic tool or paper and pencil, you are often required to make decisions based on certain basic rules and principles of mathematics. In addition, when a calculator or computer is used, you have the additional responsibility for ensuring that the tool (hardware or software) is, in fact, providing accurate and reliable results.

In this initial lesson some of the most basic mathematical concepts are reviewed. These concepts, though basic and supposedly simple, often lead to periods of frustration and hair pulling when ignored or overlooked. The basics to be presented in this lesson deal with determining how many figures to keep (where to truncate) and how or when to round off.

The number of digits displayed as the answer on most calculators and computers is governed by the physical properties of the instrument (e.g., many handheld calculators display only 10 digits). Determining how many digits to keep (where to truncate, or which digits to throwaway), and when and how to round are decisions that you must make. On the next page you will be asked to solve 12 problems requiring you to determine which digits to keep and when to round.

Using your calculator, provide your answers in two forms, the *complete* answer, and the *corrected* answer. In the first column (Complete) supply the complete answer obtained by performing the required function (probably an answer with 10 digits on many calculators). In the second column (Corrected), supply the answer retaining the *correct* number of digits, rounded where necessary.

Introductory Problems

Problem	Complete	Corrected
3.5+2.075=		
3.49-2.0075=		
2.0 x 307 =		
2.49 x 3.07 =		
2.074 x 4.700 =		
4.1 x 3.29875 =		
50+3.0069=		
9.4+334=		
9.4000 + 0.02 =		
0.052 + 0.0026 =		
0.00791 + 0.52 =		
0.0025 x 0.00025 =		

Now, compare your answers with those provided on page 2-9.

Approximate Numbers

Any number may be classified as exact or as approximate. An exact number is derived from the use of specific numbering systems and arithmetic rules. (For example, 12 is an exact number.) Approximate numbers are derived from measurements and calculations where rounding has been, or may he, applied.

When it is stated that 12 eggs are consumed by five people or that each person consumed 2.4 eggs, 2.4 eggs represents an approximate number. Even if the eggs were scrambled, we have no way of ensuring that each person consumed exactly 2.4 eggs.

With air pollution problems, we deal primarily with measurements. Therefore, we are dealing primarily with approximate numbers. Another way of considering approximate numbers is to acknowledge that an approximate number has some degree of error associated with it. Since the numbers being used are approximate and contain some degree of error at the outset, care must be taken to avoid introducing any more error into problems and their solutions.

The following general rules are useful in remembering the rules and calculating the values associated with approximate numbers.

Rule 1 *(General)*

In most cases, mathematical rules governing the results of an addition or subtraction operation are quite similar to one another, if not the same. Also, the rules governing the results of a multiplication or division operation are similar to one another, or the same. But the rules governing the results of addition and subtraction operations are generally quite different from the rules governing the results of multiplication and division operations.

Rule 2 *(General)*

When performing calculations with approximate numbers carry as many *digits as possible until the final result is calculated. Once the final result is calculated apply the appropriate rules for truncating and rounding.* Since the rule for *rounding* approximate numbers applies to addition, subtraction, multiplication, and division, and is easy to remember, we will look at it first.

Rounding Approximate Numbers

For the moment, we will not concern ourselves with where and how to truncate numbers. We will simply assume that the appropriate number of digits to be retained are givens in the following examples. When truncating (removing final, unwanted digits), rounding is normally applied to the last digit to be kept.

Rule for Rounding Approximate Numbers

If the value of the first digit to be discarded is less than 5, *retain the last kept digit with* no *change. If the value of the first digit to be discarded is* 5 *or greater, increase the last kept digit's value by one.*

Example: 25.0847
Assume only the first two decimal places are to be kept (the 4 and 7 are to be dropped).
Round to 25.08. Since the first digit to be discarded (4) is less than 5, the 8 is not rounded up.

Example: 25.0867
Assume only the first two decimal places are to be kept (the 5 and 7 are to be dropped).
Round to 25.09. Since the first digit to be discarded (6) is 5 or more, the 8 is rounded up to 9.

Adding and Subtracting Approximate Numbers

When adding or subtracting approximate numbers, a rule based upon precision determines how many digits are kept. In general, precision relates to the decimal significance of a number. When a measurement is given as 1.005 cm, we can say that the number is precise to the *thousandth* of a centimeter. If the decimal is removed (1005 cm) we have a number that is precise to *thousands* of centimeters. You may make a measurement in gallons or liters. Although a gallon or a liter may represent an exact quantity, the measuring instruments that are used are capable of producing approximations only. Using a standard graduated flask as an example, can you determine whether there is exactly one liter? Likely, not. In fact you would be hard pressed to verify that there was a liter to within ±1/1O of a liter. Therefore, depending upon the instruments used, the precision of a given measurement may vary.

If a measurement is given to us as 16.0 L, the zero after the decimal indicates that the measurement is precise to within 1/10 L. Given a measurement of 16.00 L, we have precision to 1/100 L. In short, the digits following the decimal indicate how precise the measurement is. Precision is used to determine where to truncate when approximate numbers are added or subtracted.

Truncating Approximate Numbers Following Addition or Subtraction

When approximate numbers are added or subtracted, the results are expressed in terms of the least precise number in the problem. Since this is a relatively simple rule to master, just one problem will be used to illustrate it.

Calculate the following and express the result in precise terms:

6.04 L + 2.8 L - 4.173 L = 4.7 L

The complete result is 4.667 L. The answer follows the rule of precision. The expressions in the problem have two, one, and three decimal places respectively. The least precise number (least decimal places) in the problem is 2.8, a value carried only to the tenths position. Therefore, the answer must be calculated to the tenths position only. Thus the correct answer is 4.7 L. (The last 6 and the 7 are dropped from 4.667 L, and the first 6 is rounded up to provide 4.7 L.)

Intro Problems I and 2 represent addition and subtraction of approximate numbers.

Problem 1: 3.5 + 2.075 =5.575 =5.6

The least precise number (3.5) is provided to one decimal place. The answer must therefore contain only one decimal and the second 5 is rounded up to 6.

Problem 2: 3.49 - 2.0075 =1.4825 =1.48

Two decimal places are represented by the least precise number (3.49). The answer is given to two decimals and the 8 is not rounded up.

Multiplying and Dividing Approximate Numbers

In multiplication and division of approximate numbers, finding the number of significant digits is used to determine how many digits to keep (where to truncate). We must first understand significant digits in order to determine the correct number of digits to keep or remove in multiplication and division problems.

Significant Digits

Generally, the digits 1 through 9 *are considered to be significant.* Thus, the numbers 123, 53,7492, and 5 contain three, two, four, and one significant digits respectively.

The digit 0 must be considered separately.

Zeros are significant when they occur between significant digits. In the following examples, all zeros are significant: 10001, 402, 1.1OO1, 50.09 (five, three, four, and four significant digits respectively).

Zeros are not significant when they are used as place holders. When used as a place holder, a zero simply identifies where a decimal is located. For example, each of the following numbers has only one significant digit: 1000, 500, 60, 0.09, and 0.0002. In the numbers 1200, 540, and 0.0032, there are two significant digits, and the zeros are not significant. W*hen zeros follow a decimal and are preceded* *by a significant digit the zeros are significant.* In the following examples, all zeros are significant: l.oo, 15.0, 4.1000, 1.90, 10.002, and 10.0400. In the example 10.002, the zeros are significant because they fall between two significant digits. In the last example, 10.0400, the first two zeros are significant because they fall between two significant digits; the last two zeros are significant because they follow a decimal and are preceded by a significant digit.

Additional illustrations of significant digits are provided in the following chart. The significant digits are underlined.

Examples		Number of Significant Digits
1	123	3
2	12300	3
3	12003	5
4	123.000	6
5	12300.0	6
6	1.0004	5
7	0.0004	1
8	0.005003	4
9	0.005300	4
10	1000.0001	8

Example 1 is pretty easy. There are three non-zero digits and no decimal places; therefore, three significant digits. Example 2 uses two zeros as "place holders" to locate the decimal.
The two zeros are not significant; thus, only three digits are significant. In example 3 the two zeros are not place holders, but part of a five-digit number; hence, five significant digits.
Example 4 contains three zeros after the decimal. The zeros follow a decimal and are preceded by three significant digits. (The zeros show precision. which is explained later.)
Example 5 is similar to the previous example. By the presence of the zero after the decimal preceded by significant digits the last zero becomes significant. Now the two zeros before the decimal become significant since they fall between significant digits.

The three zeros in example 6 follow the rule described in examples 4 and 5. The zeros in example 7 establish the position of the decimal only; therefore, they are not significant and the 4 is the lone significant digit. Example 8 uses four zeros. The first two zeros (place holders) are not significant; the other two are significant digits. In example 9, the two trailing zeros are significant because they follow a significant digit that follows a decimal. In the last example, all six zeros are significant since they all fall between significant digits.

Having determined how to count significant digits, we can now apply this information to determine where to truncate the results from multiplying or dividing approximate numbers.

Truncating Approximate Numbers Following Multiplication or Division

When approximate numbers are multiplied or divided the result is expressed as a number having the same number of significant digits as the expression in the problem having the least number of significant digits.

In other words, if you multiply a number having four significant digits by a number having two significant digits, the correct answer will be expressed to two significant digits.

Let's consider a measurement of 200 ft. Not knowing how the measurement was made, we can only know for certain that the measurement represents a distance of 200 ft or greater but less than 300 ft. There is one significant digit, and no matter what computation this measurement enters, the result is good to only one significant digit. Thus, if the problem 200 ft x 13.6 is solved, the complete answer is 2720.0 ft. The two numbers, 200 and 13.6, represent one and three significant digits, respectively. One significant digit is less than three; therefore the correct answer will be rendered to one significant digit. Thus, after rounding, the correct answer is 3000 ft.

If the measurement were made to two significant digits, such as 290 ft, we know that the measurement represents a distance of 290 ft or greater, but less than 300 ft. Again using the measurement, 290 ft x 13.6, the complete result yields 3944.0, and the correct result is 3900 ft. In this case, two significant digits are used (39). Since the first discarded digit is 4, the 39 remains.

Now let's reconsider the answers to problems 3 through 12 (on page 2-9) for the problems you worked.

Problem 3: 2.0 x 307 =614 =610

The number 2.0 represents two significant digits since the zero following the decimal follows a significant digit. The number 307 has three significant digits. The *least* number of significant digits is two. Therefore, the 4 in the answer is not significant and it is less than 5, so the answer, properly rounded to two significant digits, is 610. The 4 is dropped.

Problem 4: 2.49 x 3.07 =7.6443 =7.64

There are three significant digits in each number of the problem. The answer, expressed to three significant digits, is 7.64, keeping the decimal and dropping the two non-significant digits (43).

Problem 5: 2.074 x 4.700 =9.7478 =9.748

Again, both numbers in the problem have the same number of significant digits (four). By keeping four significant digits (9.747), truncating the 800 and rounding, we have 9.748.

Problem 6: 4.1 x 3.29875 =13.524875 =14

The numbers in this problem represent two and six significant digits, respectively. Using the fewest significant digits (two) the 13 is kept. By dropping and rounding 0.524875, the correct result is 14.

Problem 7: 50 + 3.0069 = 16.6284213 = 20

The first number, 50, has one significant digit. Therefore, the results will be expressed with the accuracy of one significant digit. The first digit to be truncated is the first 6. So, rounding the 1, the only significant digit becomes 2. The correct answer is then 20.

Problem 8: 9.4 + 3.34 =2.814371257 =2.8

Two significant digits divided by three significant digits means the answer must be calculated to two significant digits. The first digit to be discarded is the 1. The 8 remains unchanged, and the answer is 2.8.

Problem 9: 9.4000 + 0.02 = 470 = 500

The 0.02 in the problem contains the least number of significant digits, one. Remember that zeros used as place holders are not significant digits. Therefore, the 4 in the answer must be retained as the only significant digit. By dropping the 7 and rounding, the 4 becomes 5 and the answer is 500.

Problem 10: 0.052 + =0.0026 =20 =20

Here, both numbers in the problem are comprised of two significant digits. As it happens, the calculated number and the correct number are the same.

Problem 11: 0.00791 + 0.52 =0.015211538 = 0.015

Again, the least number of significant digits is two (0.52). Since the first digit to be discarded is a 2, the 5 remains unchanged and the answer is 0.015.

Problem 12: 0.0025 x 0.00025 = 0.000000625 = 0.00000063

Once again, the least number of significant digits is two. The answer yielded three significant digits, 625. The 5 is discarded, the 2 is rounded up to 3, and the answer is 0.00000063.

Reasonability

The rules for handling approximate numbers are used when there is no overriding rule or condition to be met. In all measurement work, deriving correct answers must be considered in context of the conditions that exist. For example, suppose you are provided numeric data to be processed. The results of your calculations are to be given to a technician who will adjust the airflow through a system. The calculation and raw results are as follows. What value should you give to the technician?

20.067 cfm x 12.9362 cfm + 18.00782 cfm = 14.41544426 cfm

You probably arrived at the value 14.415 cfm, which is a correct value using the rules provided.

However, if the gauge that the technician uses to adjust the airflow is calibrated in whole cubic feet per minute, what value should you provide? The numbers following the decimal are of no value so you should give the technician the value of 14 cfm. So now things are all set, or are they? With the piece of equipment being used, the manufacturer states that it is better to be on the high side rather than on the low side. So, since the mathematical results are actually more than 14 cfm, you had better give the technician a value of 15 cfm.

At this point you should see that even though 14.415 cfm is the correct mathematical result, the solution must be modified by reasonability to meet the environment and the operating conditions.

Rule* to *Meet the Conditions* of *Reasonability

This rule of common sense may be stated as follows: *Keep only those results that are reasonable (meaningful)* in *the context of the work being done and the equipment being used.*

R*emember,* generally you are not dealing with exact numbers; you are working with *approximate numbers.* With approximate numbers you must always be careful not to introduce undesirable errors into the final results. When multiple calculations are performed on approximate numbers, errors may become so large that the final results are of no value.

Practice Exercise

Answers are located in Appendix A.

I. Give the number of significant digits for each of the following:

a. 3.7 =
b. 2.06 =
c. 17.41 =
d. 0.114 =
e. 0.00134 =
f. 12000.0 =
g. 12000 =
h. 1200.001 =

2. Give the most accurate/precise number for the following calculations:

a. 1.50 + 2.317 =
b. 1.50 - 2.317 =
c. 1500 x 3.94 =
d. 1500+3.94 =
e. 1.500+3.94 =
2-8 1.0 - 6/3194

Introductory Problem Answers

Problem Complete Corrected

Problem		**Complete**	**Corrected**
I.	3.5+2.075=	5575	5.6
2.	3.49 -2.0075 =	1.4825	1.48
3.	2.0x307=	614.0	610
4.	2.49 x 3.07 =	7.6443	7.64
5.	2.074 x 4.700 =	9.7478	9.748
6.	4.1 x 3.29875 =	13.524875	14
7.	50+3.0069=	16.6284213	20
8.	9.4+3.34=	2.814371257	2.8
9.	9.4000 + 0.02 =	470	500
10.	0.052 + 0.0026 =	20	20
II.	0.00791 + 0.52 =	0.015211538	0.015
12.	0.0025 x 0.00025 =	0.000000625	0.00000063

The numbers given in the preceding chart represent the answers obtained when the correct rules for truncating and rounding are applied.

Definitions

Accuracy	A measure of the closeness of an individual measurement or the average of a number of measurements to the true value. Accuracy includes a combination of random error (precision) and systematic error (bias) components that are due to sampling and analytical operations; the EPA recommends using the terms *“precision”* and *“bias”*, rather than “accuracy,” to convey the information usually associated with accuracy. (See, Bias)
Air at EPA Standard Conditions	Air at 25°C and 760 mm Hg (29.92 in. Hg).
Air Pollution	The presence of unwanted material in the air. The term "unwanted material" here refers to material concentrations present for a sufficient time and under circumstances to interfere significantly with comfort, health, or welfare of persons, or with the full use and enjoyment of property.
Air Toxics	Also known as toxic air pollutants or hazardous air pollutants are those pollutants known to or suspected of causing cancer or other serious health problems. Health concerns may be associated with both short and long term exposures to these pollutants. Many are known to have respiratory, neurological, immune or reproductive effects, particularly for more susceptible sensitive populations such as children and the elderly. (See also, hazardous air pollutants).
Aspirator	Any apparatus, such as a squeeze bulb, fan, pump, or venturi, that produces a movement of a fluid by suction.
Atmosphere, The	The whole mass of air surrounding the earth and being composed largely of oxygen and nitrogen.
Atmosphere, An	A specific gaseous mass, occurring either naturally or artificially, containing any number of constitutents and in any proportion.
Bias	The systematic or persistent distortion of a measurement process, which causes errors in one direction (i.e., the expected sample measurement is different from the sample’s true value).
Breathing Zone	That location in the atmosphere at which persons breathe.
Chimney Effect	A phenomenon consisting of a vertical movement of a localized mass of air or other gases due to temperature/pressure differences.
Collection Efficiency	The percentage of a specified substance retained by a gas cleaning or sampling device.

Collector	A device for removing and retaining contaminants from air or other gases. Usually this term is applied to cleaning devices in exhaust systems.
Cloud	A visible dispersion occupying a discrete portion of space, with apparent boundaries.
Condensate	Liquid or solid matter formed by condensation from the vapor phase. In sampling, the term is applied to the components of an atmosphere that have been isolated by simple cooling.
Condensation	The process of converting a material in the gaseous phase to a liquid or solid state by decreasing temperature, by increasing pressure, or both. Usually in air sampling only cooling is used.
Condensoid	The particles of a dispersion formed by condensation.
Contaminant	Unwanted material.
Count Median Size	A measurement of particle size for samples of particulate matter, consisting of that diameter of particle such that one half of the number of particles is larger and half is smaller.
Cryogenic Sampling	See Sampling, Condensation.
Density	The mass per unit volume of substance.
Diffusion, Molecular	A process of spontaneous intermixing of different substances, attributable to molecular motion and tending to produce uniformity of concentration.
Dispersion	The most general term for a system consisting of particulate matter suspended in air or other gases.
Dispersoid	The particles of a dispersion.
Diurnal	The term means recurring daily. Applied to (variations in concentration of) air contaminants, diurnal indicates variations following a distinctive pattern and recurring from day to day.
Dust	A loose term applied to solid particles predominantly larger than colloidal and capable of temporary suspension in air or other gases. Dusts do not tend to flocculate except under electrostatic forces; they do not diffuse but settle under the influence of gravity. Derivation from larger masses through the application of physical force is usually implied.
Dust Fall	See Particle Fall.
Dust Loading	An engineering term for "dust concentration," usually applied to the contents of collection ducts and the emission from stacks.
Droplet	A small liquid particle of such size and density as to fall under still conditions, but which may remain suspended under turbulent conditions.
Efficiency	The ratio of attained performance to absolute performance, commonly expressed in percent.
Efficiency, Fractional	The mean collection efficiency for specific size

	fractions of a contaminant. Commonly this term has been applied to the performance of air cleaning equipment toward particulate matter in various size ranges.
Ejector	A device that uses a fluid under pressure, such as steam, air, or water, to move another fluid by developing suction. Suction is developed by discharging the fluid under pressure through a venturi.
Emissions	The total of substances discharged into the air from a stack vent, or other discrete source.
Emission Mixture	The total mixture in the outside atmosphere of emission from all sources.
Flocculation	Synonymous with agglomeration.
Flowmeter	An instrument for measuring the rate of flow of a fluid moving through a pipe or duct system. The instrument is calibrated to give volume or mass rate of flow.
Fly Ash	The finely divided particles of ash entrained in flue gases arising from the combustion of fuel. The particles of ash may contain incompletely burned fuel. The term has been applied predominantly to the gas-born ash from boilers with spreader stoker, underfeed stoker, and pulverized fuel (coal) firing.
Fog	A loose term applied to visible aerosols in which the dispersed phase is liquid. Formation by condensation is usually implied; in meteorology, a dispersion of water or ice.
Freezing Out	See Sampling, Condensation.
Fume	Properly, the solid particles generated by condensation from the gaseous state, generally after volatilization from melted substances, and often accompanied by a chemical reaction such as oxidation. Fumes flocculate and sometimes coalesce. Popularly, the term is used in reference to any of all types of contaminant, and in many laws or regulations, with the added qualification that the contaminant have some unwanted action.
Gas	One of the three states of aggregation of matter, having neither independent shape nor volume and tending to expand indefinitely.
Grab Sample	See Sampling, Instantaneous.

Hazardous Air Pollutants	Air pollutants, as defined in the Clean Air Act, may reasonably be expected to cause or contribute to irreversible illness or death. Such pollutants include asbestos, beryllium, mercury, benzene, coke oven emissions, radionuclides, and vinyl chloride. A total of 188 hazardous air pollutants are listed in section 112(b) of the Clean Air Act, as amended in 1990. (See also, Air Toxics)
Impaction	A forcible contact of particles of matter, a term often used synonymously with impingement.
Impactor	A sampling device that employs the principle of impaction (impingement). The "cascade impactor" refers to a specific instrument employing several impactions in series to collect successively smaller sizes of particles.
Impingement	The act of bringing matter forcibly in contact. As used in air sampling, impingement refers to a process for the collection of particulate matter in which the gas being sampled is directed forcibly against a surface.
Impingement, Dry	The process of impingement carried out so that particulate matter carried in the gas stream is retained upon the surface against which the stream is directed. The collecting surface may be treated with a film of adhesive.
Impingement, Wet	The process of impingement carried out within a body of liquid, the latter serving to retain the particulate matter.
Impinger	Broadly, a sampling instrument employing impingement for the collection of particulate matter. Commonly, this term is applied to specific instruments, the "midget" and "standard" impinger.
Impinger, Midget	A specific instrument employing wet impingement, using a liquid volume of 10 ml and a gas flow of 0.1 cu. ft. per min.

2-29

Impinger, Standard	A specific instrument employing wet impingement, using a liquid volume of 75 ml and a gas flow of 1 cu. ft. per min. (e.g. Greenberg-Smith Impinger).
Isokinetic	A term describing a condition of sampling in which the flow of gas into the sampling device (at the opening or face of the inlet) has the same flow rate and direction as the gas stream being sampled.
Mass Concentration	Concentration expressed in terms of mass of substance per unit volume of gas or liquid.

Mass Median Size	A measurement of particle size for samples of particulate matter, consisting of that diameter such that the mass of all larger particles is equal to the mass of all smaller particles.
Mist	A loose term applied to dispersions of liquid particles, the dispersion being of low concentration and the particles of large size. In meteorology, a light dispersion of water droplets of sufficient size to be falling.
Odor	That property of a substance affecting the sense of smell; any smell; scent; perfume.
Odor Concentration	The number of unit volumes that a unit volume of sample will occupy when diluted to the odor threshold.
Odor Unit	Unit volume of air at the odor threshold.
Odorant	Odorous substance.
Orifice Meter	A flowmeter, employing as the measure of flow rate the difference between the pressures measured on the upstream and downstream sides of the orifice (that is, the pressure differential across the orifice) in the conveying pipe or duct.
Particle	A small discrete mass of solid or liquid matter.
Particle Concentration	Concentration expressed in terms of number of particles per unit volume of air or other gas. (Note: On expressing particle concentration, the method of determining the concentration should be stated.)
Particle Fall	A measurement of air contamination consisting of the mass rate at which solid particles deposit from the atmosphere. A term used in the same sense as the older terms Dust Fall and Soot Fall but without any implication as to nature and source of the particles.
Particle Size	An expression for the size of liquid or solid particles expressed as the average or equivalent diameter.
Particle Size Distribution	The relative percentage by weight or number of each of the different size fractions of particulate matter.
Precipitation, Electrostatic	A process consisting of the separation of particulate matter from air or other gases under the influence of an electrostatic field.
Precipitation, Meteorological	The precipitation of water from the atmosphere in the form of hail, mist, rain, sleet, and snow. Deposits of dew, fog, and frost are excluded.

Precipitation, Thermal	A process consisting of the separation of particulate matter from air and other gases under the influence of a relatively large temperature gradient extending over a short distance. In the “Thermal Precipitator” (a sampling instrument), the air or gas is drawn through a narrow chamber across which extends a heated wire, particulate matter being deposited upon the adjacent collecting surface.
Precipitation, Ultrasonic	A process consisting of the separation of particulate matter from air and other gases following agglomeration induced by an ultrasonic field.
Precipitator, Electrostatic	Apparatus employing electrostatic precipitation for the separation of particles from a gas stream. The apparatus may be designed either for sampling or for cleaning large volumes of gas.
Precision	The degree of agreement of repeated measurements of the same property, expressed in terms of dispersion of test results about the mean result obtained by repetitive testing of a homogenous sample under specified conditions. The precision of a method is expressed quantitatively as the standard deviation computed from the results of a series of controlled determinations.
Pressure Static	The pressure of a fluid at rest, or in motion, exerted perpendicularly to the direction of flow.
Pressure, Velocity	That pressure caused by and related to the velocity of the flow of fluid; a measure of the kinetic energy of the fluid.
Pressure, Total	The pressure representing the sum of static pressure and velocity pressure at the point of measurement.
Pressure, Gauge	The difference in pressure existing within a system and that of the atmosphere. Zero gauge pressure is equal to atmospheric pressure.
Probe	A tube used for sampling or for measuring pressures at a distance from the actual collection or measuring apparatus. It is commonly used for reaching inside stacks and ducts.
Rotameter	A device, based on the principle of Stoke's Law, for measuring rate of fluid flow. It consists of a tapered vertical tube having a circular cross-section, and containing a float that is free to move in a vertical path to a height dependent upon the rate of fluid flow upward through the tube.

Sample, Integrated	A sample obtained over a period of time with (1) the collected atmosphere being retained in a single vessel, or (2) with a separated component accumulating into a single whole. Examples are particle sampling in which all the particles separated from the air is accumulated in one mass of fluid; the absorption of acid gas in an alkaline solution; and collection of air in a plastic bag. Such a sample does not reflect variations in concentration during the period of sampling.
Sample, Continuous	Withdrawal of a portion of the atmosphere over a period of time with continuous analysis or with separation of the desired material continuously and in a "linear' form. Examples are continuous withdrawal of the atmosphere accompanied by absorption of a component in a flowing stream of absorbent or by filtration on a moving strip or paper. Such a sample may be obtained with a considerable concentration of the contaminant, but it still indicates fluctuations in concentration that occur during the period of sampling.
Sampling	A process consisting of the withdrawal or isolation of a fractional part of a whole. In air or gas analysis, the separation of a portion of an ambient atmosphere with or without the simultaneous isolation of selected components.
Sampling, Condensation	A process consisting of the collection of one or several components of a gaseous mixture by simple cooling of the gas stream in a device that retains the condensate.
Sampling, Continuous	Sampling without interruptions throughout an operation or for a predetermined time.
Sampling, Instantaneous	Obtaining a sample of an atmosphere in a very short period of time such that this sampling time is insignificant in comparison with the duration of the operation or the period being studied.
Sampling, Intermittent	Sampling successively for limited periods of time throughout an operation or for a predetermined period of time. The duration of sampling periods and of the intervals between are not necessarily regular and are not specified.
Series Collection	An operation involving the use of two or more collectors joined in a series.
Settling Velocity	The terminal rate of fall of a particle through a fluid as induced by gravity or other external force; the rate at which frictional drag balances the accelerating force (or the external force).

Smog	A term derived from smoke and fog, applied to extensive atmospheric contamination by aerosols which arise partly through natural processes and partly from the activities of human subjects. Now sometimes used loosely for any contamination of air. (See also, Photochemical Smog)
Smog, Photochemical	Air contamination caused by chemical reactions of pollutants formed primarily by the action of sunlight on oxides of nitrogen and hydrocarbons.
Smoke	Small gas-borne particles resulting from incomplete combustion, consisting predominantly of carbon and other combustible material, and present in sufficient quantity to be observable independently of the presence of other solids.
Sorbent	A liquid or solid medium in or upon which materials are retained by absorption or adsorption.
Sorption	A process consisting of either absorption or adsorption or both.
Specific Gravity	The ratio of the density of the substance in question to the density of a reference substance at specified conditions of temperature and pressure.
Temperature, Absolute	(a) Temperature measured on the thermodynamic scale, designated as degrees Kelvin (K). (b) Temperature measured from absolute zero (-273.15°C or - 459.67 °F). The numerical values are the same for both the Kelvin scale and the ideal gas scale.
Vapor	The gaseous phase of matter which normally exists in a liquid or solid state.
Volume Concentration	Concentration expressed in terms of gaseous volume of substance per unit volume of air or other gas, usually expressed in percent or parts per million.

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Chapter 3

Standard Methods for Criteria Pollutants

This chapter identifies the standard methods for the measurement of the criteria pollutants.

Introduction

To protect the public health from harmful air pollution, the 1970 Amendments to the Clean Air Act (CAA) authorized the US 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.

3.1 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 3-1.

Table 3-1. 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 μg/m^3	Quarterly Average	Same as Primary		High-Volume sampling with AA analysis	same
Nitrogen Dioxide	0.053 ppm (100 μg/m^3)	Annual (Arithmetic Mean)	Same as Primary		Gas-phased Chemiluminescence	same
Particulate Matter (PM$_{10}$)	150 μg/m^3	24-hour(2)	Same as Primary		High- or Low-Volume Sampling	same
Particulate Matter (PM$_{2.5}$)	15.0 μg/m^3	Annual(3) (Arithmetic Mean)	Same as Primary		Low-Volume Sampling	same
	35 μg/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 μg/m3.

(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 $\leq$ 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 maybe 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 EPA Course 435 Student Manual, Chapter 4, *Particulate Matter Sampling*.

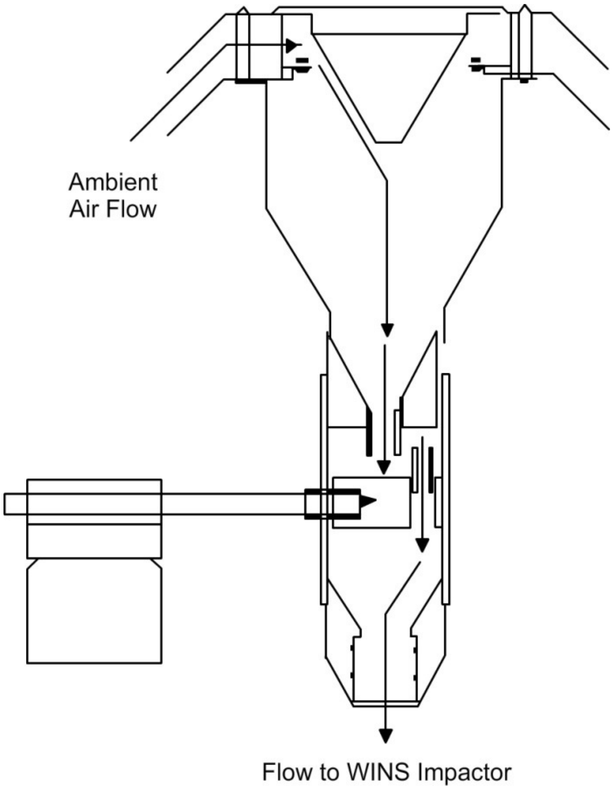


Figure 3-1. Schematic image of PM2.5 sampler utilizing a WINS Impactor.

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. There are PM_{10} samplers which utilize particle size separators which differ from the configuration shown in Figure 3-2 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 ($\mu g/std\ m^3$).

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 EPA Course 435 Student Manual, Chapter 4, *Particulate Matter Sampling*.

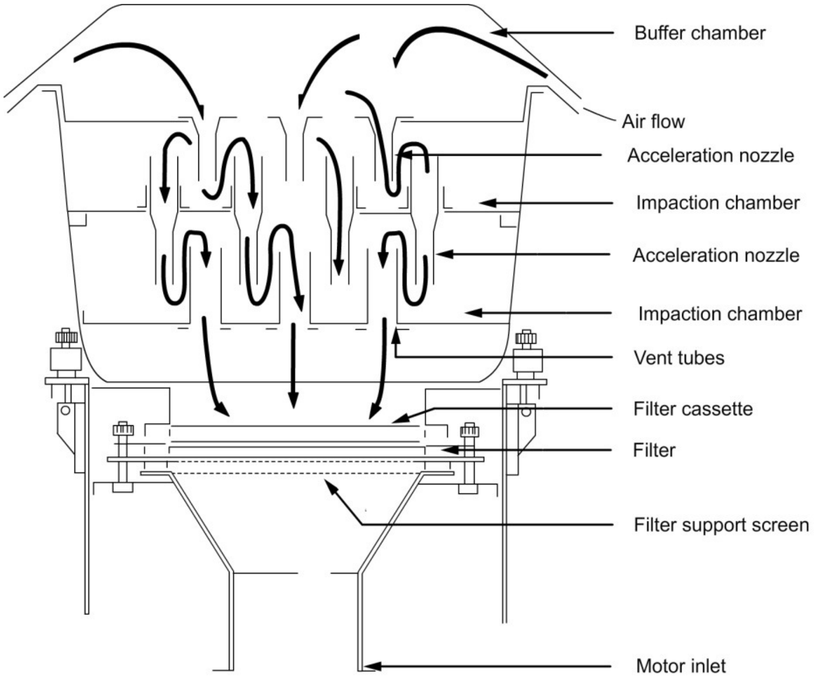


Figure 3-2. Schematic of PM_{10} sampler.

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 3-3.

Ozone monitoring locations now use the equivalent method, which is an ultraviolet method.

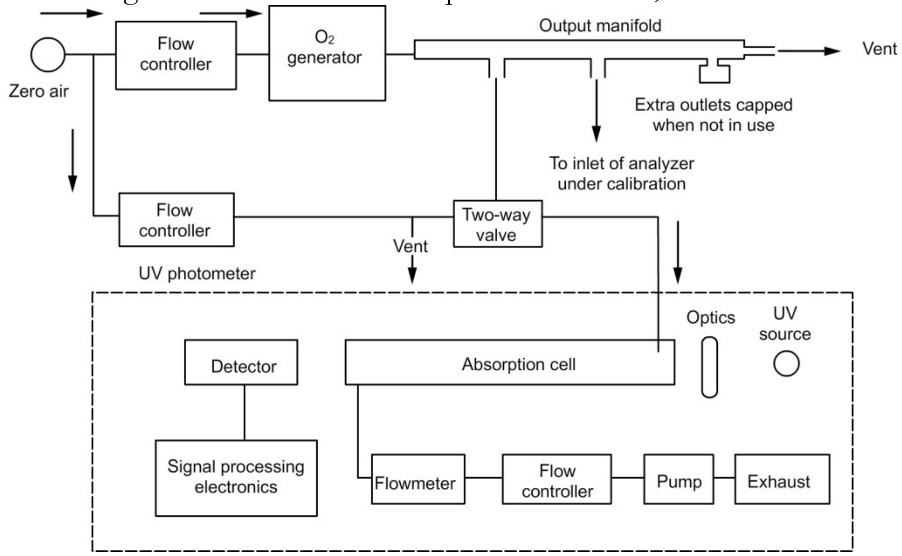


Figure 3-3. Schematic diagram of a typical photometric calibration system.

A more details discussion of ozone monitors and the generation of test atmospheres for their calibration can be found in Chapters 6 and 7 of this Student Manual.

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 details discussion of carbon monoxide monitors and the generation of test atmospheres for their calibration can be found in Chapter 8 of this Student Manual.

Nitrogen Dioxide

The reference measurement principle for the determination of nitrogen dioxide is the gas-phase chemiluminescence reaction of nitric oxide with ozone (Eq. 3-1).

(Eq. 3-1)

$$NO + O_3 \rightarrow NO_2 + O_2 + hv\,(light)$$

Nitrogen dioxide is measured indirectly by measuring total oxides of nitrogen $(NO_x = NO_2 + NO)$ 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. 3-2).

(Eq. 3-2) $NO_2 + catalytic\ converter \rightarrow NO + O$

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. 3-3).

(Eq. 3-3) $NO + O_3 \rightarrow NO_2 + O_2$

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 details discussion of nitrogen dioxide monitors and the generation of test atmospheres for their calibration can be found in Chapter 3 of this Student Manual.

Sulfur Dioxide

The reference method for the measurement of Sulfur 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 3-2.

Table 3-2. 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 relate to the sampling train (Figure 3-4) 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.

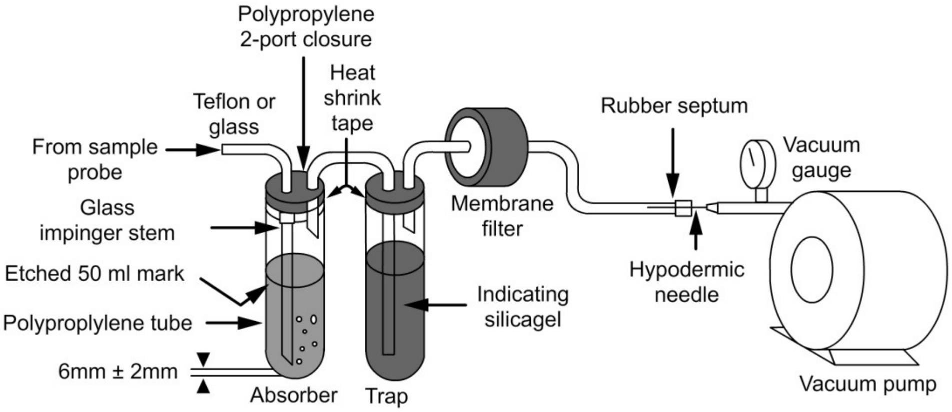


Figure 3-4. SO_2 sampling train for 24-hour sampling.

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 is 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 details discussion of sulfur dioxide monitors and the generation of test atmospheres for their calibration can be found in Chapter 5 of this Student Manual.

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 details discussion of lead monitors can be found in EPA Course 435 Student Manual, Chapter 4, *Particulate Matter Sampling* and Chapter 8 – *Introduction to Sampling for Air Toxics*.

References

The Clean Air Act.

U.S. Environmental Protection Agency. 40 CFR Pt. 50, Appendix A (July 1, 1997).

U.S. Environmental Protection Agency. 40 CFR Pt. 53.

U.S. Environmental Protection Agency. 42 Fed. Reg. 1271-1289 (December 14, 1977).

U.S. Environmental Protection Agency. 43 Fed. Reg., no. 194, pp. 46258-46261 (October 5, 1978).

U.S. Environmental Protection Agency. 40 CFR Pt. 58.

U.S. Environmental Protection Agency. *Quality Assurance Handbook for Air Pollution Measurement Systems*. (EPA 454/R-98-004).

Ambient Monitoring Technology Information Center. http://www.epa.gov/ttn/amtic

Chapter 4

Generation of Standard Test Atmospheres

Introduction

Calibration of atmospheric sampling equipment is very important for air monitoring, and it must be done to ensure that the data generated by air monitors represent the actual concentration of pollutants in air. Many factors may affect the calibration of sampling or monitoring devices, preventing them from providing a true measure of the atmospheric contaminant concentrations. The generation of standard test atmospheres is essential to the calibration procedures for continuous air monitoring instrumentation.

There is a need for reliable, accurate methods to generate pollutant gases of known concentration. For example, an air monitor may be designed to operate at certain efficiency, but due to factors such as reagent deterioration, electrical or electronic component variability, and flow rate changes, data generated by an air monitor may differ from the true concentration of a pollutant in air. To evaluate the performance of sampling equipment, *known* contaminant concentrations must be introduced; by knowing the input concentration, the output of the monitor can be determined for accuracy. The purpose of this section is to discuss the methods of preparing gases of known concentration.

The most important factor in the preparation of these standard atmospheres is devising a method of preparing gases of known concentration. Moreover, in the preparation of the standard atmospheres, devising a method of creating accurate calibration gases at the extremely small concentrations typically found in the atmosphere is necessary. Atmospheric testing often requires calibration concentrations in the sub-part-per-million, or –billion levels.

Static Systems

Pressurized Systems

Pressurized systems are frequently used in the laboratory to produce large volumes of gas mixture. Technically speaking, a pressurized system is a dynamic method since the usual procedure is to mix moving gas streams. However, the process of making and storing mixtures of gases in an appropriate cylinder is generally termed a static method when preparing calibrated gas mixtures.

Although pressurized tanks of known contaminant concentrations are usually purchased, they may be prepared by the following procedures. Cylinders containing a pollutant gas are prepared by adding a known volume of pollutant gas and then pressurizing the cylinder with a diluent gas. The gas is then of known concentration and can be used for calibration purposes. The range of concentrations that can be achieved by this method is typically less than 100 ppm to more than 5000 ppm, depending on the stability of the gaseous pollutant. The concentration of the mixture can be calculated as follows:

(Eq. 4-1)
$$Cppm = \frac{10^6\ x\,V_c}{V_d + V_c} = \frac{10^6\,p_c}{p_t}$$

Or

(Eq. 4-2)
$$C_{\%} = \frac{10^2\ x\,V_c}{V_d + V_c} = \frac{10^2\,p_c}{p_t}$$

Where: C_{ppm} = concentration of gas mixture, ppm by volume
$C_{\%}$ = concentration of gas mixture, percent
V_c = volume of contaminant gas
V_d = volume of diluents gases
p_c = partial pressure of contaminant gas
p_t = total pressure of gas mixture

Using the rigid container procedure to pressurize a gas cylinder with a known concentration of a contaminant gas of interest, it is necessary to construct a gas-handling manifold that interconnects the vacuum source, the calibrated volume, the source of contaminant gas, and the gas cylinder. Subsequently, the entire system is evacuated; the known calibration volume is flushed and filled at atmospheric pressure with the contaminant gas and isolated, and connecting lines are again evacuated. The contaminant gas is then swept by diluent carrier gas into the cylinder, and the cylinder is pressurized with diluent gas to the desired pressure. Because of compressional heating, the cylinder should be allowed to equilibrate at room temperature before reading the pressure to be used in the concentration calculations. The concentration of the mixture is calculated as follows:

(Eq. 4-3)
$$C_{ppm} = \frac{10^6\ x\ V_c\ x\ P_b}{V_{cyl} + V_c}$$

Where: C_{ppm} = concentration of gas mixture, ppm by volume
V_c = volume of pure contaminant gas
V_{cyl} = volume of cylinder
P_b = barometric pressure at time of filling
P_t = final total pressure of cylinder

One factor that must be watched closely when preparing gas mixtures by this method is the thoroughness of the mixing. When introducing the gases into the cylinder one at a time, a layering effect may occur and result in incomplete mixing. This effect can be counteracted by allowing for adequate mixing time before use.

It should be noted that at room temperature and pressure most gas mixtures conform closely to the ideal gas law. However, at the higher pressures that is present in the cylinders, gaseous mixtures can deviate from this law and create errors of up to 20%. This can be corrected by using a quantity called the compressibility factor (B). The units for the pressure and volume are not important as long as P_c and P_t are in the same units and V_c and V_d are in the same units, since both parts-per-million and percent are unit-less quantities.

In commercial practice, compressed gas cylinders of calibration gases are often prepared using high load mass balances; in this procedure, a precise tare weight for an evacuated cylinder is obtained, and the cylinder is weighed again following the addition of the desired trace constituent and after the addition of the diluent gas (prepurified nitrogen in most cases) under pressure. The mass fraction of the contaminant gas is converted to a volumetric concentration by application of the usual formula involving molecular weight and molar volume.

When prepared by the user, a pressure dilution technique of some sort is generally necessary. Here the volume of the contaminant gas introduced, V_c, the volume of the cylinder, V_{cyl}, the evacuation pressure, P_{vac}, and the final total pressure in the cylinder, P_t, must be known.

As a matter of good practice, cylinders should be continued in the same service and not interchanged; for example, a cylinder formerly used for SO_2 span gas should not be converted to NO_2 service. Further, cylinder materials consistent with the gases to be contained therein should be used.

In general, ambient monitoring instruments should be calibrated by allowing the instrument to sample and analyze test atmospheres of known concentrations of the appropriate pollutant in air. All such (non-zero) test concentrations must be, or be derived from, local or working standards (e.g., cylinders of compressed gas or permeation devices) that are certified as traceable to a NIST primary standard. "Traceable" is defined in 40 CFR Parts 50 and 58 as meaning " ... *that a local standard has been compared and certified, either directly or via not more than one intermediate standard, to a primary standard such as a National Institute of Standards and Technology Standard Reference Material (NIST SRM) or a USEPA/NIST approved Certified Reference Material (CRM)".* Normally, the working standard should be certified directly to the SRM or CRM, with an intermediate standard used only when necessary. Direct use of a CRM as a working standard is acceptable, but direct use of an NIST SRM as a working standard is discouraged because of the limited supply and expense of SRM's. At a minimum, the certification procedure for a working standard should:

- establish the concentration of the working standard relative to the primary standard;
- certify that the primary standard (and hence the working standard) is traceable to an NIST primary standard;
- include a test of the stability of the working standard over several days; and,
- specify a recertification interval for the working standard.

A detailed discussion of cylinder gas preparation and traceability can be found in, *EPA Traceability Protocol for Assay and Certification of Permeation Device Calibration Standards,* EPA-600/R-97/121, 1997. This protocol describes two procedures for assaying the concentration of compressed gas calibration standards and for certifying that the assayed concentrations are traceable to a National Institute of Standards and Technology (NIST) Standard Reference Material (SRM).

This protocol is mandatory for certifying the compressed gas calibration standards used for the pollutant monitoring that is required by the regulations of 40 CFR Parts 50, 58, 60 and 75 for the calibration and audit of ambient air quality analyzers and continuous emission monitors (see Table 4-1). This protocol may be used by specialty gas producers, standard users, or other analytical laboratories.

TABLE 4-1. Certification periods for compressed gas calibration standards in aluminum cylinders that are certified under this protocol.

Certified components	**Balance gas**	**Applicable concentration range**	**Certification period (months)**
Ambient nonmethane organics (15 components)	Nitrogen	5 ppb	24
Ambient toxic organics (19 components)	Nitrogen	5 ppb	24
Aromatic organic gases	Nitrogen	≥0.25 ppm	36
Carbon dioxide	Nitrogen or air [a]	≥300 ppm	36
Carbon monoxide	Nitrogen or air	≥8 ppm	36
Hydrogen sulfide	Nitrogen	≥4 ppm	12
Methane	Nitrogen or air	≥1 ppm	36
Nitric oxide	Oxygen-free nitrogen [b]	≥4 ppm	24
Nitrous oxide	Air	≥300 ppb	36
Oxides of nitrogen (i.e., sum of nitrogen dioxide and nitric acid)	Air	≥80 ppm	24
Oxygen	Nitrogen	≥0.8%	36
Propane	Nitrogen or air	≥1 ppm	36
Sulfur dioxide	Nitrogen or air	40 to 499 ppm	24 [c]
Sulfur dioxide	Nitrogen or air	≥500 ppm	36
Multicomponent mixtures	—	—	See text
Mixtures with lower concentrations	—	—	See text

Note a: When used as a balance gas, "air" is defined as a mixture of oxygen and nitrogen where the min. concentration of oxygen is 10 % and the concentration of nitrogen is greater than 60 %.

Note b: Oxygen-free nitrogen contains <0.5 ppm of oxygen.

Note c: <6 months for Precursor Gas-level SO_2 STDS.

Rigid Chambers

Rigid chambers such as the one illustrated in Figure 4-1 are another method of preparing an analytical gas standard, in the laboratory for immediate use as a test atmosphere.

The gaseous contaminant is introduced into the vessel, mixed with the diluent gas, and sampled. The volume of the chamber may vary with the type of application, but the principle remains the same. Preparation of standard gas mixtures by this procedure has been largely replaced by more accurate permeation devices and pressurized cylinders containing a specified pollutant concentration.

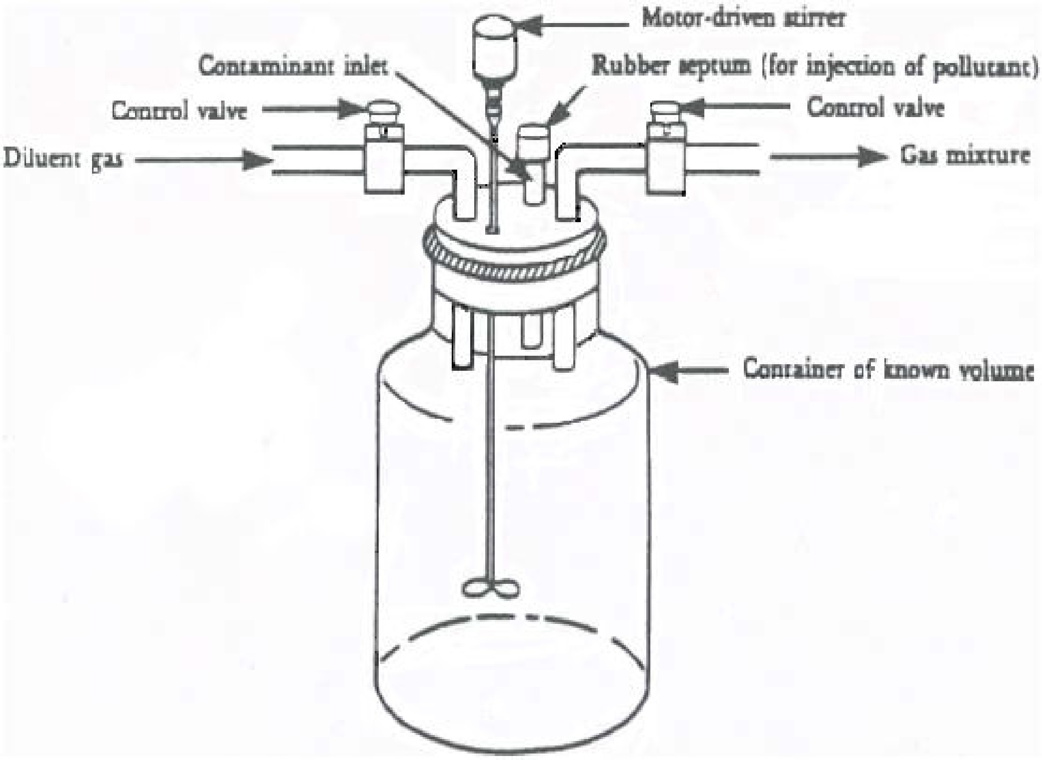


Figure 4-1. Rigid chamber used for producing standard gas mixture.

As the gas mixture is withdrawn and replaced by diluents air the contaminant concentration within the chamber decreases as a function of time. This relationship is described in the following equation.

(Eq. 4-4) $$C_{t=x} = C_o \, e^{-t\left(\frac{v}{V}\right)}$$

Where: $C_{t=x}$ = Concentration at time, x

C_o = Initial Concentration at time, zero

t = time

v = volume withdrawn

$\mathcal{V}$ = volume of static chamber

Nonrigid Chambers-Bag Samples

In this procedure, a bag, usually of a flexible, nonreactive plastic material, is filled with a known volume of diluent gas, and a known volume of contaminant gas is added to the system. The diluent gas should be cleaned of all interfering constituents and be nonreactive to the desired contaminant. After allowing for complete mixing in the bag, a sample can be drawn off for calibration purposes. The concentration of contaminant in the bag mixture can be calculated by (if the initial contaminant concentration is 100%):

$$c_{ppm} = \frac{V_c}{V_d + V_c} \tag{Eq. 4-5}$$

Where: c_{ppm} = concentration of diluted contaminant, ppm by volume

V_c = volume of contaminant gas, ul

V_d = volume of diluent gas, l

One of the first and most important steps in this preparation is the selection of the bag. The bag must be of a flexible material and be chemically inert to the gases it will contain. Chemical inertness is very important; if the contaminant gas reacts with the bag, the amount of contaminant will decrease and the actual concentration of the bag mixture will be unknown. Teflon®, Mylar® and copolymer Tedlar® bags have been widely used because they are inert to most materials. Before any bag is to be used, it should be tested with the contaminant gas to be sure that no reaction will take place between the bag and the gas. After the bag has been selected, it should be checked for leaks, particularly the seams of the bag and the area around the valve, before the sample is introduced. The bag should be flushed and evacuated at least three times to ensure that all unwanted contaminants have been removed.

The actual filling of the bag must be done under controlled conditions to guarantee measurement of the volume. Clean air is pumped into the bag through an accurately calibrated flowmeter. The flow rate of the diluent gas must be kept as constant as possible throughout the filling procedure to obtain an accurate measure of volume. After the flow rate is set, a stopwatch is used to get an accurate filling time. The product of the flow rate and the filling time is the total volume of diluent gas added to the system.

The contaminant sample should be introduced into the stream of diluent gas as the bag is filling. This should be done after the bag has filled to about one-quarter of the desired volume. By introducing the sample at this time, mixing can take place as the bag fills to its final volume. The sample is introduced into the diluent gas stream with the use of a syringe. A rubber septum and tee assembly is located in the filling line for insertion of the syringe. Care must be used when handling the syringe to ensure that the desired quantity of contaminant is introduced.

The syringe should have a graduated barrel so that the amount of contaminant entered can be read directly. The plunger of the syringe must be gas-tight so no sample will escape while being injected into the diluent gas stream. A Teflon™ cap can be fitted over the plunger to eliminate gas escaping during introduction. The sample gas is extracted with the syringe from a source of known concentration. When drawing the sample, the syringe should be filled and evacuated at least six times with the sample gas to eliminate any air that may have been present in the needle. The plunger of the syringe should be drawn well past the desired volume when entering the sample. Just before introducing the sample into the diluent gas stream, the syringe should be adjusted to the desired volume to eliminate any error from air that may have diffused into the needle. Care should be taken in handling the syringe; it should never be held by the barrel or the needle. Heat from the hand of an analyst will cause the gas in the syringe to expand and part of the sample will be lost from the needle. When introducing the sample, the tip of the needle should be in the middle of the diluent gas stream to prevent the sample from being lost on the walls of the filling lines. After depressing the plunger, remove the needle from the gas stream immediately to ensure that none of the sample will diffuse out of the needle and into the gas stream, giving a higher resulting concentration. Mixing time can be decreased by kneading the bag for several minutes.

The concentration of the calibration gas will change during storage. The decay rate will depend upon the substance being stored, the relative humidity, and the bag material. Substances such as nitrogen dioxide and ozone will decay faster than carbon monoxide and hydrocarbons. Figure 4-2 illustrates the rate of decay with time of a known concentration of SO_2 stored in a bag. The decay rate can be decreased if the bag is preconditioned. The preconditioning required that the bag be flushed several times with the sample gas. The bag should be left overnight at least once with a sample gas in it as a preconditioning step.

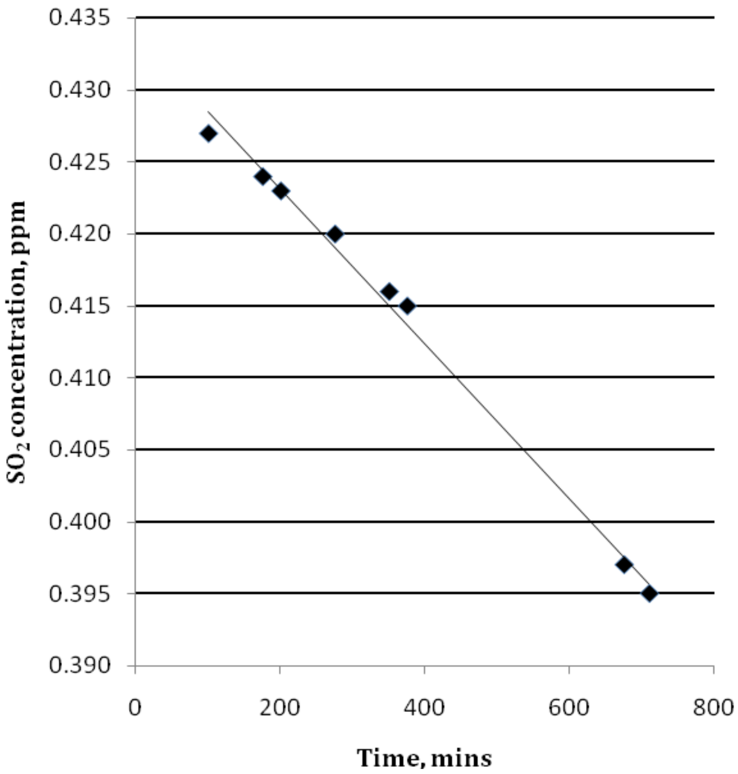


Figure 4-2. Rate of decay of SO2 concentration in a bag.

Polasek and Bullin (1978) found that sample stability depends clearly on the compound and type of bag material used. Table 4-2 gives the results of carbon monoxide deterioration with time in bags of various materials.

Table 4-2. Carbon monoxide sample deterioration with date in bags of various materials.

Bag material	**pvc**	**Tedlar**	**Snout®**	**Aluminized polyester**
No. of bags tested	**10**	**10**	**5**	**3**
Concentration of calibration gas used to fill bags, ppm	9.0	9.0	8.2	8.2
0 h after filling, avg ppm	8.9	8.5	8.2	8.0
Avg deviation, ppm	- 0.12	- 0.5	0	-0.17
Avg sqd deviation, ppm²	0.056	0.352	0.012	0.030
24 h after filling, avg ppm	8.5	7.5	8.0	7.9
Avg deviation, ppm	- 0.50	- 1.5	-0.16	-0.30
Avg sqd deviation, ppm²	0.306	4.2	0.048	0.097
48 h after filling, avg ppm	8.4	6.8	8.3	8.2
Avg deviation, ppm	- 0.63	- 2.2	0.10	-0.03
Avg sqd deviation, ppm²	0.497	7.7	0.010	0.010
100 h after filling, avg ppm	7.9	5.2	8.0	7.7
Avg deviation, ppm	- 1.2	- 3.8	-0.18	-0.50
Avg sqd deviation. ppm²	1.5	17.8	0.066	0.25

*Consists of layers of polyester. polyvinyl chloride, aluminum. polyamide, and polyethylene.

Dynamic Systems

Permeation Systems

The use of permeation techniques for preparation of standard mixtures is very useful for some contaminants. The method is based on the theory that a gas confined above its liquefied form at a constant temperature will permeate through some materials at a constant rate. By putting a liquefied gas into a Teflon® tube, for example, permeation of the vapor through the tube will take place because of the concentration gradient that exists between the inner and outer tube walls. By passing different flows of diluent gas over the tube, gases of varying concentration can be generated.

The actual concentration of a sample gas at the EPA's standard temperature and pressure -STP (25°C, 760 mm Hg) can be calculated by Equation 4-5.

(Eq. 4-5)

$$C_{ppm} = \frac{(PR)\left(\frac{24.45}{MW}\right)}{Q_t}$$

Where: c = concentration, ul/l or ppm by volume

PR = permeation rate, ug/min

Q_t = total flow rate, corrected to STP, std l/min

MW = molecular weight of the permeation gas, ug/u-mole

24.46 = molar volume ($\overline{V}$) of any gas at STP, ul/u-mole

Permeation tubes allow for the generation of gases with concentrations in the sub-part-per-million range. Permeation tubes are made from a variety of different materials. The material must allow the diffusion of the contaminant gas through the walls and also be inert to the diffusing gas. If some reaction took place between the tube material and the gas, the permeation rate would be affected and might no longer be constant. Teflon®, Mylar®, and Saran Wrap® are materials often used because of their chemical inertness and good permeation properties. Before any material is used for the permeation tube, it should be tested to ensure that no changes will occur in the material when it comes in contact with liquefied gas. To test the material, a piece should be placed in some of the liquefied gas it will contain. The material should be removed after a few days and checked to see if any changes in-the material have occurred (i.e., brittleness, holes, stickiness, etc.). If there are no apparent changes, the material is probably suitable for use.

The first step in the construction of the tube is to compress the desired sample gas to a liquid state. The liquefied gas is then put into a tube and the tube ends are sealed. One method of sealing the tube ends is to force glass beads or stainless steel balls into the tube ends. To seal properly, these beads should be approximately one and one-half times the inside diameter of the tube. Once the tube has been prepared, it should be stored for at least 36 hours in order to equilibrate. Since the permeation rate is extremely dependent on temperature and relative humidity, the permeation tube should be stored at a constant temperature with dry air or nitrogen passing over it. After equilibration, the permeation rate of the tube can be determined either gravimetrically or by use of a calibrated analyzer.

For the gravimetric determination, the tube should be weighed on an analytical balance and replaced in the storage area. Time required to weigh the tube should be minimized and kept constant to compensate for the effects of moisture absorption. High humidity will cause the permeation tube to absorb moisture, thereby increasing the tube weight. This will yield an erroneously low value for the permeation rate. Absorbed moisture on the tube can form acids that may cause tube blistering, thus changing the permeation rate. The tube should be stored and weighed several times to yield enough data to demonstrate that the permeation rate is constant. The results of these weightings should be plotted on a graph as weight versus time. From the slope of the resulting best "fit" line, the permeation rate can be calculated in micrograms per minute as shown in Figure 4-3. Mathematically, the slope can be calculated by dividing the change in weight of the permeation tube by the change in time. A more precise permeation rate can be determined from the data, weight and elapse time, by performing linear regression of the paired values.

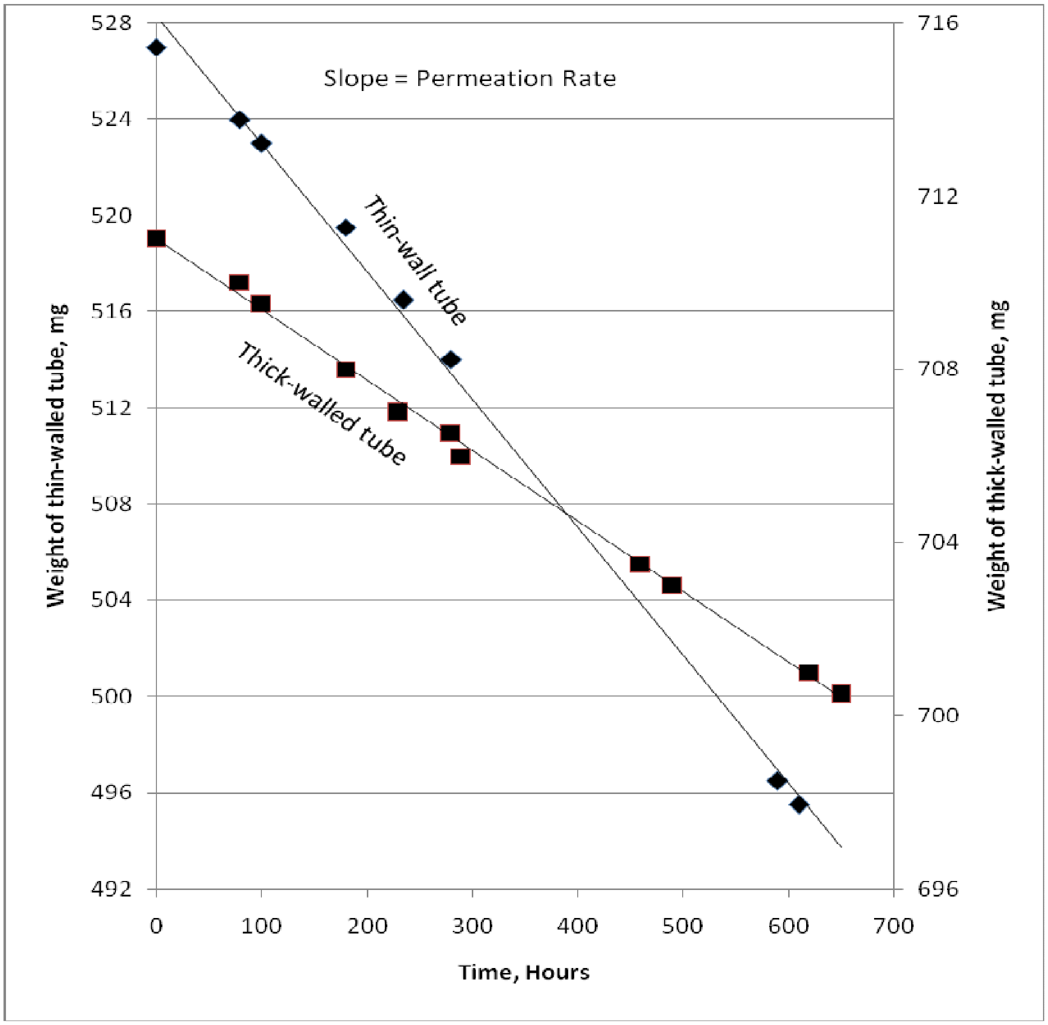


Figure 4-3. Calibration of two permeation tubes.

This protocol describes three procedures for assaying the permeation rate of a permeation device calibration standard and for certifying that the assayed permeation rate is traceable to National Institute of Standards and Technology (NIST) reference standards. This protocol is mandatory for certifying the permeation device calibration standards used for the pollutant monitoring that is required by the regulations of the Code of Federal Regulations, Chapter 40, Parts 50 and 58 for the calibration and audit of ambient air quality analyzers. This protocol covers the assay and certification of sulfur dioxide (SO_2) and nitrogen dioxide (NO_2) permeation device calibration standards. This protocol may be used by permeation device producers, standard users, or other analytical laboratories. The assay procedure may involve the comparison of these standards to permeation device reference standards (i.e., Procedure P1), to compressed gas reference standards (i.e., Procedure P2), or to mass reference standards (i.e., Procedure P3).

The permeation device reference standards that may be used under this protocol are NIST Standard Reference Material (SRM) numbers 1625 and 1626. These SRMs (listed in Table 4-3) are permeation tubes containing SO_2. In the future, NIST may develop additional SRMs, which may be used as reference standards under this protocol (*EPA TRACEABILITY PROTOCOL*

FOR ASSAY AND CERTIFICATION OF PERMEATION DEVICE CALIBRATION STANDARDS, 1997).

TABLE 4-3. NIST SRM PERMEATION DEVICE REFERENCE STANDARDS

NIST SRM no.	**Permeation device type**	**Device length (cm)**	**Nominal permeation rate at 30 °C (μg/min)**	**Nominal concentration (in μmol/mol) at various dilution gas flow rates (L/min)**		
				1	5	10
1625	Sulfur dioxide	10	3.7	1.4	0.28	0.14
1626	Sulfur dioxide	5	2.1	0.8	0.16	0.08

Once the tube has been calibrated, it can be used to generate test gases of known concentration. The permeation tube is placed in a stream of diluent gas. The gas passes over the tube and the permeated gas is mixed into the gas stream. The desired concentration can be varied by varying the flow rate of the diluent gas. The diluent gas must be kept at a constant temperature during the time the calibration gas is being generated to be sure the permeation rate is constant. The temperature dependence of the permeation rate is illustrated for four gases in Figure 4-4. To accomplish this, the diluent gas is drawn through a constant temperature chamber before passing over the tube as in Figure 4-5.

Permeation tubes are commercially available from many sources offering a variety of precalibrated tubes with different permeation rates. The NIST offers some reference sources. A number of configurations other than the original tube design are also commercially available. Some of these are designed to provide a longer useful life.

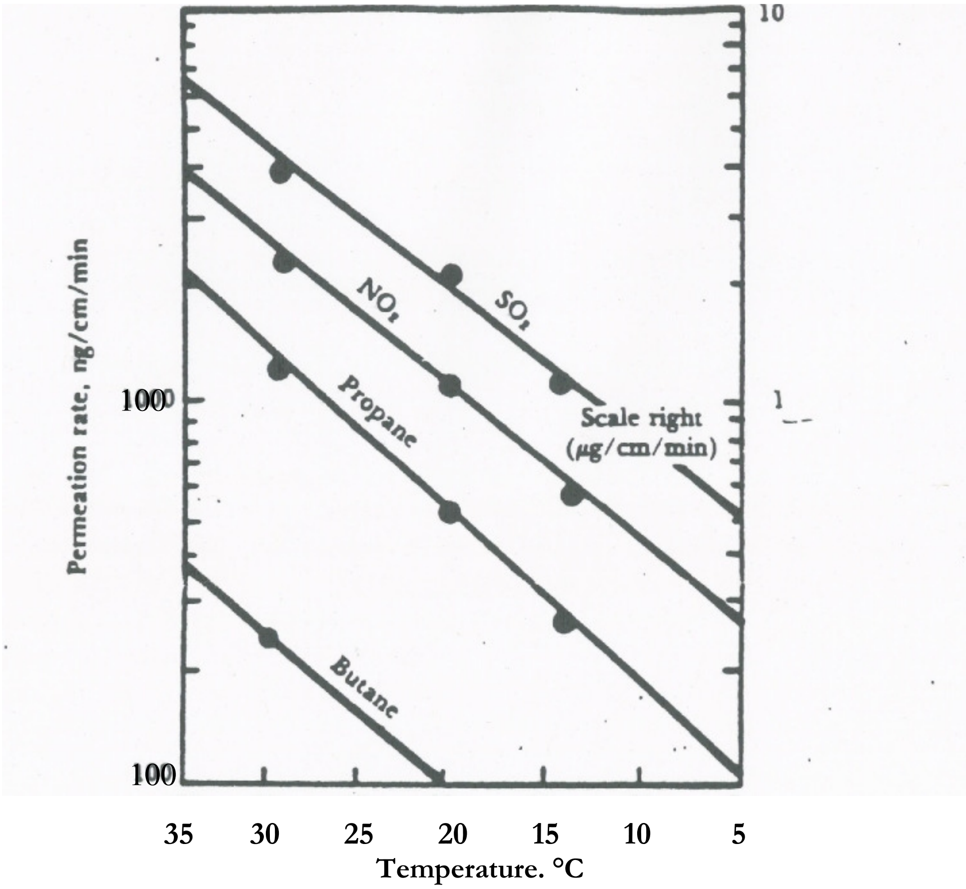


Figure 4-4. Permeation rate vs. temperature for four gases.

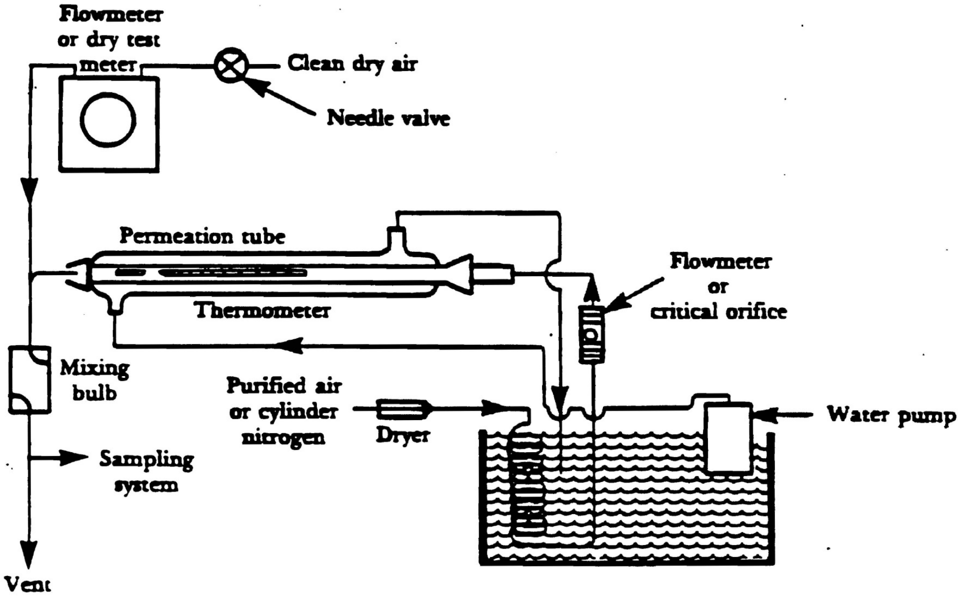


Figure 4-5. Components and flow of a typical permeation system.

The performance of a permeation device depends on the polymer films used to construct these tubes and the pollutant for which a standard concentration is needed. The important factors to be considered in the use of a permeation device are temperature, humidity, gas stability, equilibration time, etc. These parameters have been studied for nitrogen dioxide, sulfur dioxide, and recently for numerous halogenated hydrocarbons and for permeation tubes constructed with FEP (fluorinated ethylene propylene copolymer) Teflon®.

Types of Permeation Devices

Tubular device

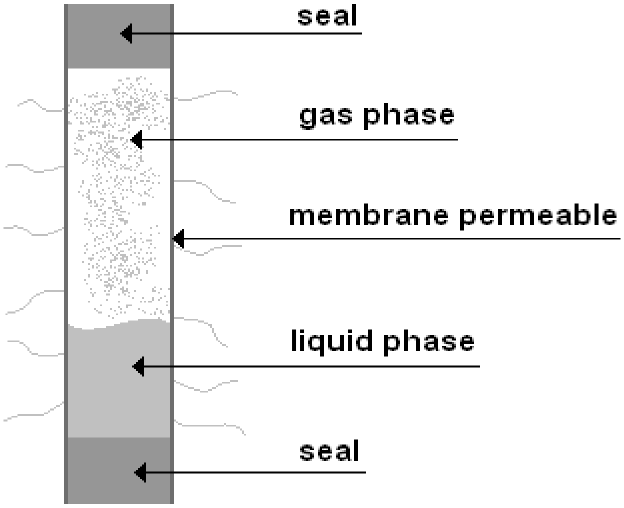
The tubular device, as shown in Figure 4-6, is a sealed permeable cylinder containing the desired permeant gas. Release of the chemical occurs by permeation through the walls of the Teflon® tube for the entire length between the impermeable plugs. A wide range of rates can be achieved by varying the length and thickness of the tube, with typical rates ranging from 5 ng/min to 50,000 ng/min.

Extended life tubular device

An extended life tubular device is essentially a standard permeation tube coupled to an impermeable stainless steel reservoir. The range of permeation rates corresponding to the standard tubular device, but has a significantly enhanced lifetime – by a factor of 3 for a 5 cm (active length) device or a factor of 12 for a 1 cm device.

Wafer device

Wafer devices have only a small permeable window, or wafer, so permeation rates are typically an order of magnitude lower than rates for tubular devices. Since permeation occurs only through the polymeric wafer, the permeation rate is controlled by varying the wafer material, the thickness of the wafer, and the diameter of the permeation opening. Gases whose high vapor pressures at normal permeation temperatures prevent their containment in a tubular device can be contained in a wafer device. Wafer devices are available in different styles to allow use in calibrators made by various manufacturers.



Courtesy, Fine Permeation Tubes - Nuova Grangiara, Italy

Figure 4-6. Permeation tube (tubular).

The tubular type of permeation device is the most commonly used for the calibration of ambient air monitors. To determine the rate of permeation in this type of device, the tube may simply be removed from the permeation system and weighed to the nearest 0.1 mg on an analytical balance. Generally weightings can be made daily, weekly, or monthly, depending on the gas and type of permeation device. As indicated previously, the permeation rate can be determined by measuring the slope of the least-squares error line used to fit the weight vs. time data. A more rapid calibration, however, can be obtained by using the apparatus shown in Figure 4-7.

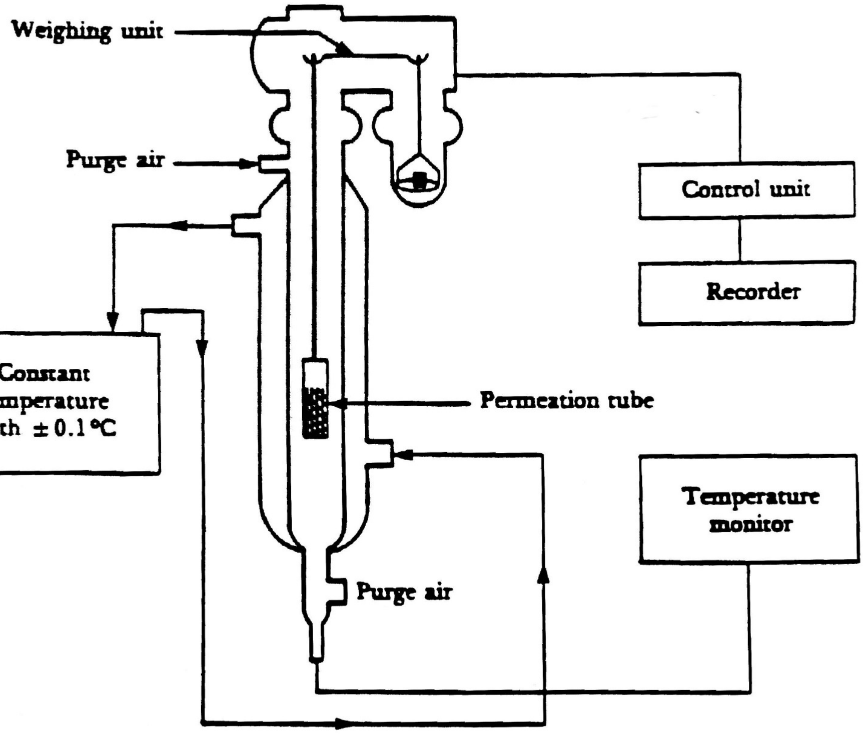


Figure 4-7. Gravimetric calibration apparatus.

In addition to rapid calibration, this apparatus has the advantage of continuous direct read-out of weight change (Figure 4-8), and the permeation tube is maintained in the constant temperature bath at all times. The potential problem of spurious weight increase due to the hygroscopic nature of some pollutants (e.g., SO, NO_2) is eliminated with this device, for the tube need never have to leave the constant temperature bath. Today, a Multi-gas Dynamic Calibrator (Figure 4-9) with an optional internally plumbed permeation oven is the preferred device when using a permeation tube to create a test atmosphere.

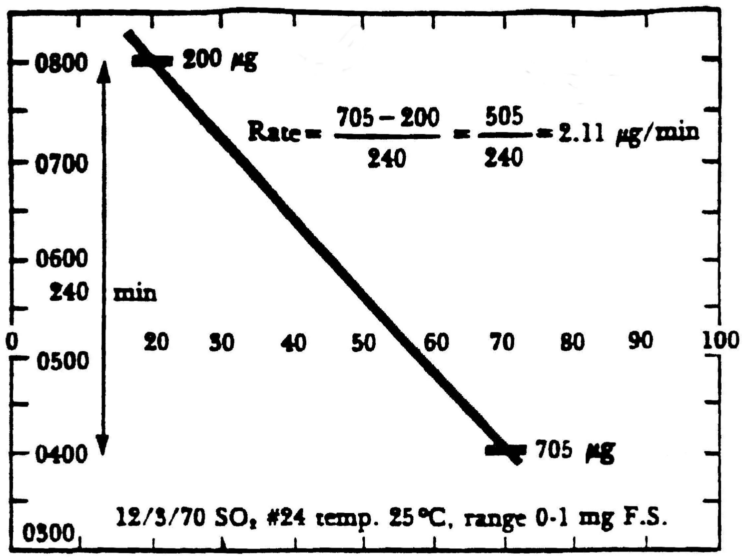


Figure 4-8. Typical strip chart read-out from an in situ thermal-gravimetric apparatus.

Dilution Systems

The calibration standards used for the calibration of ambient air analyzers can be generated by dilution of a commercially-prepared and certified compressed gas standard using a mass flow controlled (MFC) calibration unit. The method of generating calibration standards by dilution involves the accurate measurement of the constituent gas flow rate and the diluent gas flow rate prior to blending these gas streams.

The calibration unit includes mass flow controllers that are based upon small thermistors that are sensitive to heat loss. A potential voltage is applied to the thermistor and, as the gas flow increases across the thermistor, the resistance of the thermistor changes proportionally with the flow rate. This change in resistance can be measured very accurately by electronic circuitry and a feedback loop within the MFC circuitry monitors the gas flow and controls the flow rate to maintain the desired rate.

Using two channels in parallel, the MFC calibrator unit controls the constituent gas flow rate and the diluent gas flow rate such that upon mixing these gases generates a working standard (test atmosphere) with the desired concentration. Typical flow ranges of the MFC units are up to 10 L/min for the diluent gas flow and up to 100 cm^3/min for the constituent gas flow. These systems allow for accurate dilution of standard gases from high concentration to low ambient working standard concentrations. When the constituent concentration in the commercially-prepared standard cylinder is certified by reference to NIST standards, and the MFCs are calibrated to NIST-traceable standards, the resulting working standard concentration is considered to be NIST-traceable.

It is important a MFC calibrator meets the 40 CFR 50 requirements of ±2 percent flow accuracy and that the calibrations of both MFC channels be checked periodically using a NIST traceable flow standard. Routine MFC flow rate checks must be standard procedure. To accomplish such check, a NIST traceable flow standard must be available as part of every calibration system.

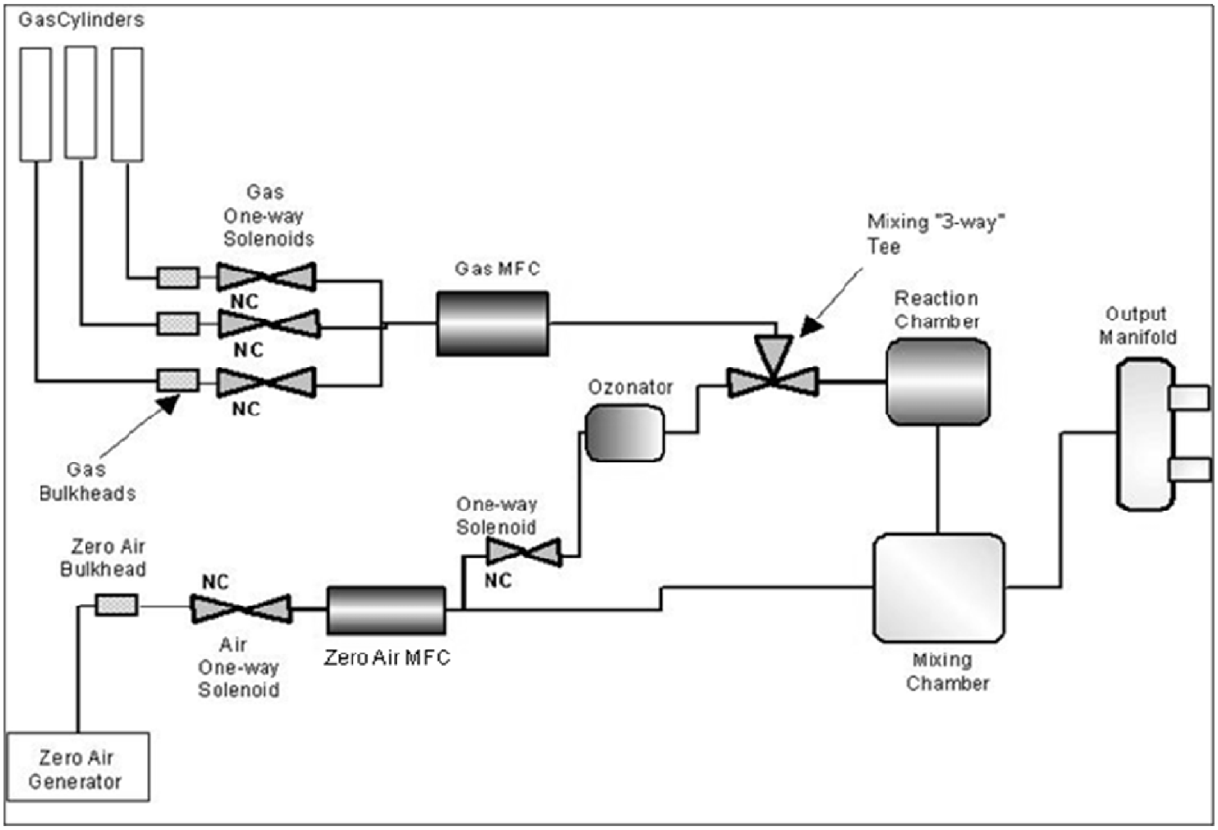


Figure 4-9. Schematic of a typical Multi-gas Dynamic Calibrator equipped with Mass Flow Controllers.

A simple system for diluting gas entails mixing the gas with the diluent in a mixing chamber after measuring their flow rates. A dilution system using a dynamic calibrator utilizing MFCs to measure flow is illustrated in Figure 4-9. The concentration of the test mixture can be calculated with the following formula:

(Eq. 4-6) $$c_u Q_u = c_d (Q_u + Q_d)$$

Where:

c_u = concentration of undiluted contaminant gas (concentration in the gas cylinder)

c_d = concentration of diluted test mixture (desired concentration to challenge the analyzer)

Q_u= flow of undiluted contaminant gas

Q_d =flow of diluent gas (e.g. zero air).

Rearranging,

(Eq. 4-7) $$c_d = \frac{c_u Q_u}{(Q_u + Q_d)}$$

Since the concentrations values for the constituent gas, c_u, and the desired test mixture, c_d, are known, Equation 4-7, is rearranged to solve for the flow rates of the constituent gas and the diluent gas (i.e. zero air). Substitute, $Q_t = (Q_u + Q_d)$.

(Eq. 4-8) $$Q_t = \frac{c_u Q_u}{c_d}$$

Since, there are 2 unknowns in this relationship, Q_t and Q_u, the process used to solve this equation is somewhat more complicated than if there were only 1 unknown. The simplest process to solve for the flow rates (unknowns) is to first select a reasonable flow rate for the constituent gas based on the available flow rate range of the flow measuring device (i.e. MFC for the constituent gas). On a modern multi-gas dynamic calibrator, a typical flow rate range for the constituent gas is 0-100 cc/min (0-0.100 liters/min). Based on such a range it would be reasonable to select a flow rate for the constituent gas, Q_u, of 50 cc/min. It is then possible to solve for, Q_t. The diluent gas flow rate (i.e. zero air) can then determined by subtracting, Q_u, from, Q_t, ($Q_d = Q_t - Q_u$). Subsequently, flow rates can be calculated for each of the multi-point concentrations required to "challenge" the analyzer under calibration. As the constituent gas flow rate is varied, to achieve the desired test concentration, it is necessary to maintain the diluent gas flow rate within the allowable range. A typical flow rate range for the diluent gas is 0-10 liters/min.

It is important to know the sample flow rate demand for the instrument under calibration to ensure there is sufficient flow rate generated as a test atmosphere. For example, if the instrument under calibration samples at 1 liter per minute. The test atmosphere flow rate leaving the dynamic calibration must exceed the instrument flow rate "demand" of 1 liter per minute. It is recommended that it exceed the instrument sample flow rate by 20% or more.

Flow measuring devices other than rotameters, are frequently used to increase the accuracy and precision of the test mixture concentration. The most common and precise flow measuring device used is the mass flow meter or mass flow controller.

The Multi-gas Dynamic Calibrator illustrated in Figure 4-9 is equipped with an ozonator which can be engaged on the zero air line to provide for Gas Phase Titration (GPT). GPT is one of 2 methods for calibration of the NO_2 channel of a NO-NO_2-NO_x analyzer. GPT is discussed in detail in Chapter 9, *Oxides of Nitrogen Measurement Principle and Calibration Procedure.*

Ozone Generation

Ozone is unlike most of the gaseous pollutants in that there are no gaseous calibration standards available. This is due to ozone's instability, which makes it impossible to produce gas cylinders of standardized ozone concentrations or ozone permeation tubes. The only means available for the calibration of ozone monitors is to produce stable, known amounts of ozone at the site of calibration.

Ozone is most commonly produced by irradiating oxygen with an ultraviolet light source in an ozone generator. An ozone generator may utilize a tubular quartz chamber into which ozone-free air is admitted at a controlled, constant rate. This incoming air (from a zero air source) is subjected to ultraviolet radiation from a mercury vapor lamp.

Ozone can be generated by irradiating zero air with UV light from a cold cathode mercury vapor lamp. To be useful for calibration, the generated ozone concentrations must be stable and reproducible over a 15- to 30-minute time period. The ozone concentration can be modulated in several ways: (1) increasing or decreasing the intensity of the lamp to raise or lower the ozone concentration while keeping the air flow constant; (2) increasing or decreasing the air flow while keeping the lamp intensity constant; and (3) mechanically altering the intensity of the radiation using a variable shutter or sleeve. Most commercially available calibration systems with internal ozone generators modulate the ozone concentration by changing the intensity of the generating lamp electronically.

Preparation of Zero Air

Introduction

Zero air can be defined as air that is free of contaminants and interferences for a particular analysis technique. It is important to note that a zero air for one analysis may not be a zero air for another analysis. For example, an analysis technique may require a zero air that has only sulfur dioxide and water vapor removed while another analysis technique may call for only hydrocarbons to be removed. It is important to understand the zero air composition requirements provided for in the particular method being applied.

Zero gases are used extensively in atmospheric sampling, both in laboratory and field applications. Many continuous monitors require a constant supply of zero air for parallel path reference cells. Cylinder air can be used, but by applying the proper adsorption or, absorption column on the inlet gas stream, zero gas can be continuously produced from atmospheric air. This can cut costs and eliminate the necessity of replenishing zero air cylinders.

Zero Gas Generators are commercially available and if properly equipped and operated can provide a cost-effective and appropriate supply of zero air. The important considerations in selecting a zero air generator are as follows:

Compression: The zero air source should be at an elevated pressure to allow accurate and reproducible flow control and to aid in subsequent operations such as drying, oxidation, and scrubbing. An air compressor that gives an output of 10 psig is usually sufficient for most applications.

Drying: Several drying methods are available. Passing the compressed air through a bed of silica gel, using a heatless air dryer, or removing water vapor with a permeation dryer are three possible approaches.

Oxidation: Carbon Monoxide (CO) and Nitric oxide (NO) are usually oxidized to CO_2 and NO_2, respectively, in order to ease scrubbing. Oxidation can be accomplished by either ozonation or chemical contact. During ozonation, the air is passed through an ozone generator. The O_3 that is produced reacts with the NO to form NO_2. Care must be taken to allow sufficient residence time for the ozonation reaction to go to completion.

Chemical oxidation is accomplished by passing the air stream through a reacting bed. Such agents as CrO_3 on an alumina support or Purafil® are very efficient at oxidizing NO to NO_2. A mixture of copper and manganese oxides or Hopcalite® is typically used to oxidize CO to CO_2. The chemical contact approach has the advantage of needing no electrical power input for its application.

Scrubbing: The last step in the generation of the zero air is the removal of the remaining contaminants by either further reaction or absorption. Fixed bed reactors are usually employed. The following materials (figure 4-4) have been shown to be effective:

Table 4-4. Scrubbing Materials

To Remove	Use
NO_2	Soda-Lime (6-12 mesh), Purafil
Hydrocarbons	Molecular Sieve (4A), Activated Charcoal
O_3 and SO_2	Activated Charcoal

Contaminants and their typical concentrations found in clean, dry ambient air are summarized in Table 4-5.

Table 4-5. Typical composition of clean, dry air near sea level.

Component	Formula	Content	
		% by Volume	ppm
Nitrogen	N_2	78.09	780,900
Oxygen	O_2	20.94	209,400
Argon	Ar	0.93	9,300
Carbon dioxide	CO_2	0.033	330
Neon	Ne	18×10^{-4}	18
Helium	He	5.2×10^{-4}	5.2
Methane	CH_4	1.5×10^{-4}	1.5
Krypton	Kr	1.0×10^{-4}	1.0
Hydrogen	H_2	0.5×10^{-4}	0.5
Nitrous oxide	N_2O	0.5×10^{-4}	0.5
Xenon	Xe	0.08×10^{-4}	0.08
Ozone *	O_3	0.03×10^{-4}	0.03
Ammonia	NH_4	0.01×10^{-4}	0.01
Iodine	I_2	0.01×10^{-4}	0.01
Nitrogen dioxide	NO_2	0.001×10^{-4}	0.601
Sulfur dioxide	SO_2	0.0002×10^{-4}	0.0002
Carbon monoxide	CO	0 to trace	-

*Ozone content in winter is 0.02 ppm and in summer is 0.05 ppm.

There are many techniques for producing zero air. The purpose of this section is to discuss the most widely used methods for removing contaminants from a gas stream to produce a zero air. It should be noted that water vapor is a contaminant that must be removed from many gas streams. This is especially true when introducing a gas stream into a permeation tube system where the gas must be free of water vapor. This ensures proper permeation through the walls of the permeation tube. For this reason, a separate discussion of drying a gas stream is provided in this section.

Gaseous Contaminant Removal

There are many ways of removing a gaseous contaminant from a gas stream, including the use of catalytic devices, adsorption, and absorption. Table 4-6 lists the more commonly used materials.

Table 4-6. Materials used in producing zero air up to 30 liters per min.

Material	Purpose	Comments
Activated charcoal	Removes many gases such as ozone, SO_2, NO_2, higher molecular weight organic vapors. Does not completely remove CO and CO_2.	Typically, the activated charcoal 6 x 16 mesh is contained in a 2 inch I.D. x 15 inch long clear plastic cartridge. Glass wool plugs with a perforated support to retain charcoal in place. This type of container is commercially available. Containers of other materials and similar configuration and volume may be used.
NO oxidizer		
a. potassium permanganate (Purafil®)	Converts NO to NO_2 for subsequent removal with activated carbon or soda lime.	Typically, the Purafil® pellets are contained in a 2 inch I.D. x 15 inch long clear plastic cartridge. Glass wool plugs with a perforated support to retain charcoal in place. This type of container is commercially available. Containers of other materials and similar configuration and volume may be used. Unlike activated carbon and silica gel, Purafil® cannot be regenerated.
b. Chromium trioxide (CrO_2)	Converts NO to NO_2 for subsequent removal with activated carbon, or soda lime.	Soak firebrick or alumina 15-40 mesh in a solution containing 16 g CrO_2 in 100 ml of water. Pass dilute NO air stream over water at a fixed temperature such that the humidity of the air stream is maintained within 50 ± 20% RH.
Desiccant (silica gel)	Removes water	The 6 x 16 mesh silica gel with color indicator is, typically, contained in a 2 inch I.D. x 15 inch long clear plastic cartridge. Glass wool plugs with a perforated support to retain charcoal in place. This type of container is commercially available. Containers of other materials and similar configuration and volume may be used. When the change in color exceeds ¾ of the desiccant bed depth, regenerate by exposing the silica gel to 120°C atmosphere overnight.
Carbon monoxide Oxidizer (Hopcalite)	Catalytically oxidizes CO to CO_2 for subsequent removal with activated carbon, Ascarite or soda lime	Commercial mixture of copper and manganese oxides. Hopcalite is contained in a 2 inch I.D. x 15 inch long clear plastic cartridge. Glass wool plugs with a perforated support to retain charcoal in place. This type of container is commercially available. Containers of other materials and similar configuration and volume may be used.

Material	Purpose	Comments
CO_2 absorber	Removes CO_2, H_2O	a. Soda lime: commercial preparation of calcium and sodium hydroxides: 4 to 8 mesh. b. Ascarite[e] (on silica) Soda Lime or Ascarite® is contained in a 2 inch I.D. x 15 inch long clear plastic cartridge. Glass wool plugs with a perforated support to retain charcoal in place. This type of container is commercially available. Containers of other materials and similar configuration and volume may be used.

Catalytic Devices

Catalytic devices have been used to selectively remove a gas from the sample stream. This leaves a reference or zero gas that is minus only the pollutant to be measured. Using this method, the change in output when the catalyst bed is bypassed will be due only to the pollutant measured. An example of a specialized catalytic conversion is the UV absorption ozone monitor. Ozone is selectively removed from the sample using a manganese dioxide catalyst that reduces ozone to oxygen. This ozone-free sample, which still contains all other gases, is the reference, or zero, air for the UV ozone monitor and is used as the baseline. The gas stream then bypasses the catalyst, and the ozone-carrying gas enters the monitor where the change in output can be attributed specifically to the ozone.

Adsorption

Adsorption is a widely used method for removing contaminants from a gas stream to form a reference, or zero, air. Solid adsorbents have the ability to absorb quantities of gases because they have extremely high surface areas per unit weight; e.g., activated carbon has a surface area ranging from 300 to 1400 m^2/gm. A more detailed discussion of the porous quality of adsorbents may be found in the literature. Table 4-7 lists the properties of some common adsorbents.

Table 4-7. Typical properties of adsorbents.

Adsorbent	Form	External surface Area, Ft2/lb	Pore volume Ft2/lb	Reactivation Temp., ^{o}F	Max. gas Flow, CFH/Ib	Sp. heat, Cp BTU/(lb^{o}R)	Typical adsorbates
Activated	Pellets	10.5-21.5	0.010 -	200 -1000	/	0.25	CH_4 through n-C_6H_{12}
carbon	Beads (G)	15.0-24.0	0.013	200-1000	/	0.25	CO_2, H_2S
Silica gel	Beads (G)	5.0-16.0	0.007	250-450	75	0.22	CH_4 through
	Beads (S)	6.0		300-450	75	0.25	C_5H_{10}, C_2H_4 through C_4H_8
							H_20, H_2S, SO_2
Activated	Beads (G)	7.0-18.5	0.006	350-600	50	0.22	H_2S, SO_2
alumina	Beads (S)	4.0- 8.0		350-1000	50	0.25	Oil vapors
Molecular	Pellets	9.0-14.5	/	300-600	/	0.23	See Tables 6-9
sieves							6-10, and 6-11
	Beads (G)	32.0	/	300-600	/	0.23	
	Beads (S)	7.5-12.5	/	300-600	/	0.23	

Note (G) = Granules, (S) = Spheroids

Activated carbon and molecular sieves are the most widely used solid adsorbents for the removal of contaminants. Activated carbon has been used extensively for the adsorption of many contaminant gases in a sample stream not only in atmospheric sampling and in laboratory use but also as an industrial adsorbent in continuous flowing adsorption beds. The term "activated" carbon derives from a method of enhancing the adsorption properties of regular carbon. The carbon is "activated" by heating at 900 °C in a reducing atmosphere to increase the porous nature of the carbon, thereby increasing the adsorbency of the carbon. Activated carbon can be made from many substances including soft coal, fruit pits, nut shells, and coconut shells. Coconut shell carbon is the desired form of activated carbon because of its porous nature. Table 6-8 lists the adsorptive capacity of activated carbon for several gases.

Table 4-8. Adsorption of gases by carbon (1 gm of adsorbent, temperature 15°C).

Gas	Volume adsorbed, cm^2
SO_2	380
CH_4Cl	277
NH_3	181
H_2S	99
HCl	72
C_2H_2	49
CO_2	48
CH_4	16
CO	9
O_2	8
N_2	8
H_2	5

Molecular sieves are also widely used as adsorbents because of their porous nature. Unlike filtration, molecules small enough to pass through the pores are adsorbed while larger molecules are not. The molecular sieves are usually made from synthetic zeolite crystals, metal aluminosilicates, clays, porous glasses, microporous charcoals, zeolites, active carbons, or synthetic compounds that have open structures through which small molecules, such as nitrogen and water can diffuse. The diameter of the pores or passageways of the molecular sieve regulates the size of the molecules that may pass through the sieve. Because of this, molecular sieves have been used extensively in the fractionation of organic gases (hydrocarbons) as packing material in gas chromatographic columns. Various properties of molecular sieves are summarized in Tables 4-9, 4-10, and 4-11.

Table 4-9. Molecular sieve adsorption characteristics.

Adsorbed on 4A and 5A molecular sieve	Adsorbed on 5A but not 4A molecular sieve	Not adsorbed on 5A or 4A molecular sieve
Water	Propane and higher n-paraffins to C_{14}	Isobutane and all iso-paraffins
CO_2		
CO^*	Butene and higher n-olefins	Isopropanol and all iso-sec- and tert-alcohols
H_2S		
SO_2	n-butanol and higher n-alcohols	Benzene and all aromatics
NH_3		
NO_2^*	Cyclopropane Freon 12	Cyclohexane and all cyclics with at least 4 numbered rings
O_2^*		
CH_4^*		
Methanol		
Ethane		Carbon tetrachloride Sulfur hexafluoride Hexachlorobutadiene Freon 114 and 11
Ethylene		
Acetylene		
Propylene		
n-Propanol		Boron trifluoride Molecules larger than 5 Å
Ethylene oxide		

* = adsorbed below - 20°F.

Å = angstrom, unit of length that is internationally recognized, equal to 0.1 nanometer (nm) or 1×10^{-10} m, meaning 1/10,000,000,000 meters. It is sometimes used in expressing the sizes of atoms, lengths of chemical bonds and visible-light spectra. In everyday terms, a sheet of paper is approximately 1,000,000 angstroms thick. Visible light covers the range from 4,000 to 8,000 angstroms.

Table 4-10. Molecular sieves-Linde type.

Type	Nominal pore diameter, µm	Molecules adsorbed*	Remarks
3 A	0.003	<3 Å effective diameter (e.g.. H_2O, NH_3)	Used for drying and dehydration
4 A	0.004	<4 Å diameter (e.g., H,S,, ethanol. CO,. SO,. C,H., and C2H)	Scavenge water from solvents and sat. hydrocarbons (HC)
5 A	0.005	<5 Å diameter (e.g., n-C.H,-OH C,H, to C,,H..)	Separates n-paraffins from branched and cyclic HC
10X	0.008	<8 Å diameter (e.g., iso-paraffin and olefins, C.H.)	Separates aromatic HC
13X	0.010	<10 Å diameter	Drying, H_2S and mercaptan removal (gas sweetening)

*Each type adsorbs listed molecules plus those of preceding types.

Table 4-11. Effective sorption capacities of molecular sieves.

Zeolite	Amount sorbed @ 25°C (g/ 100g of molecular sieve)		
	H_2O	n-C_7H_{14}	Cyclohexane
4 A	24.5	-	-
5 A	24.5	12.0	-
B	20.0	-	-
X	31.5	16.8	18.5
Y	28.0	16.5	19.0
Erionite	11.3	4.4	6.7
Offretite	16.6	8.6	5.3
Mordentite	13.3	6.1	7.3

Methods for regeneration of molecular sieves include pressure change, heating and purging with a carrier gas, or heating under high vacuum.

Absorption

Absorption is also a means of removing unwanted gases from the sample stream. One absorptive method could be much like the sampling of gases through impingers: the contaminant could be scrubbed from the system using a liquid solution. Solid absorbents are also used. Levaggi et al. (1972) discuss a method of absorbing nitrogen dioxide from a gas stream by using triethanolamine on firebrick. This will selectively absorb nitrogen dioxide while allowing the passage of nitric oxide.

Water Vapor Removal

As mentioned previously, water vapor removal is very important in the preparation of calibration gases using permeation tubes. Water vapor removal is also important when using some catalysts or adsorbents. For example, water vapor must be removed before passing a gas stream over a bed of Hopcalite, because water vapor causes Hopcalite to lose its oxidizing properties. There are many other situations where water vapor must be removed. The four most widely used laboratory and air sampling methods of removing water vapor (drying) from a gas stream are adsorption, absorption, condensation, and permeation.

Adsorption

Adsorption of water vapor on solid desiccants is the most common method of drying a gas stream. This is because solid desiccants are readily available, easy to handle and store, can be regenerated, and can be prepared with an indicator material in them that changes color when the desiccant is spent.

The choice of a drying agent should not be based solely on its drying ability. Other factors, such as stability, temperature dependency, ability to perform in high humidity situations, emission of gases through reaction with the moisture, etc., should be taken into account.

The three most widely used drying adsorbents are silica gel, calcium sulfate, and anhydrous magnesium perchlorate. Efficiency and capacities of these and other solid desiccants are listed in Tables 4-12 and 4-13.

Table 4-12. Comparative efficiency of various drying agents.

Material	Volume of air per hr per ml desiccant, ml	Total vol. of air per ml of desiccant, liters	Residual water vapor per liter of air, mg
$CuSO_4$ (anhy.)	36 to 50	0.45 to 0.7	1.8 (2.7-2.9)
$CaCI_2$ (gran.)	66 to 165	6.1 to 24.2	1.5 (1.4-1.6)
$CaCI_2$ (tech. anhy.)	115 to 150	4.0 to 5.8	1.25 (1.23-1.27)
$ZnCl_2$ (sticks)	120 to 335	0.8 to 2.1	0.98 (0.94-1.02)
$Ba(CIO_4)_2$ (anhy.)	26 to 36	2.5 to 3.7	0.82 (0.76-0.88)
NaOH (sticks)	75 to 170	2.3 to 8.9	0.80 (0.78·0.83)
$CaCl_2$ (anhy.)	75 to 240	1.2 to 7.8	0.36 (0.33-0.38)
$Mg(CIO_4)_2 \cdot 3H_2O$	65 to 160	4.0 to 7.2	0.031 (0.028-0.033)
Silica gel	65 to 135	6.5 to 7.7	0.03 (0.02-0.04)
KOH (sticks)	55 to 65	3.2 to 7.2	0.014 (0.010-0.017)
AI_2O_3	65 to 135	6.5 to 7.7	0.005 (0.004-0.009)
$CaSO_4$ (anhy.)	75 to 150	1.2 to 18.5	0.005 (0.004-0.006)
CaO	60 to 90	7.6 to 10.1	0.003 (0.003-0.004)
$Mg(C1O_4)_2$ (anhy.)	95 to 130	6.4 to 13.2	0.002 (0.002-0.003)

BaO	64 to 66	10.6 to 25.0	0.00065 (0.006-0.0008)

Table 4-13. Comparative efficiencies and capacities of various solid desiccants in drying a stream of nitrogen.

Desiccant	Initial composition	Regeneration requirements		Average Efficiency [b] (mg/liter)	Relative Capacity [c] (liters)
		Drying time (hr)	Temperature (°C)		
Sodium hydroxide [a]	$NaOH \cdot 0.03\ H_2O$	-	-	0.513	178
Anhydrous barium perchlorate	$Ba\ (ClO_4)_2$	16	127	0.599	28
Calcium oxide	CaO	6	500, 900	0.656	51
Magnesium oxide	MgO	6	800	0.753	22
Potassium hydroxides [g]	$KOH \cdot 0.52\ H_2O$	-	-	0.939	18.4
Mekohbite [g]	68.7% NaOH	-	-	1.378	68
Anhydrous magnesium perchlorate [d]	$Mg(ClO_4)_2 \cdot 0.12\ H_20$	48[e]	245[e]	0.0002	1168
Anhydrone [d, f]	$Mg(ClO_4)_2 \cdot 1.48\ H_2O$	-	240	0.0015	1157
Barium oxide	96.2% BaO	-	1000	0.0028	244
Activated alumina	Al_2O_3	6 to 8	175, 400	0.0029	263
Phosphorus pentoxide [g]	P_2O_5	-	-	0.0035	566
Molecular sieve 5A [f]	Calcium aluminum silicate	-	-	0.0039	215
Indicating anhydrous magnesium perchlorate [d]	88% $Mg(ClO_4)_2$and 0.86% $X.MnO_4$	48[e]	240[e]	0.0044	435
Anhydrous lithium perchlorate [g]	$LiClO_4$	12[e], 12	70[e], 110	0.013	267
Anhydrous calcium chlorides [j]	$CaCl_2 \cdot 0.18\ H_20$	16[e]	127[e]	0.067	33
Drierite [f]	$CaSO_4 \cdot 0.02\ H_2O$	1 to 2	200 to 225	0.067	232
Silica gel	-	12	118 to 127	0.070	317
Ascarite [f]	91.0% NaOH	-	-	0.093	44
Calcium chloride [g]	$CaCl_2 \cdot 0.28\ H_2O$	-	200[e]	0.099	57
Anhydrous calcium chlorides [g]	$CaCl_2$	16 [e]	245[e]	0.137	31
Anhydrocel [f]	$CaSO_4 \cdot 0.21\ H_2O$	1 to 2	200 to 225	0.207	683

Note a: Nitrogen at an average flow rate of 225 ml/min was passed through a drying train consisting of three Swartz drying tubes (14 mm i.d. by 150 mm deep) maintained at 25°C.

Note b: The average amount of water remaining in the nitrogen after it was dried to equilibrium.

Note c: The average maximum volume of nitrogen dried at the specified efficiency for a given volume of desiccant.

Note d: Hygroscopic.

Note e: Dried in a vacuum.

Note f: Trade name.

Note g: Deliquescent.

Silica gel is easy to handle, and it can readily and indefinitely be regenerated at temperatures near 120°C. Attempting to regenerate silica gel above 260°C will cause loss of the water vapor extractive properties. More often, a series of adsorbents are used for drying a gas stream. A popular series method for water vapor removal is silica gel followed by molecular sieve. The silica gel, which can be regenerated easily, removes a major portion of the water vapor, and then the molecular sieve, which is a more efficient drying agent, removes most of the remaining water vapor.

Calcium sulfate also has excellent regenerative capabilities (1 to 2 hours at 200°C); however, unlike silica gel, it will gradually lose its drying properties because of the destruction and reformation of the dehydration elements. Calcium sulfate is also able to operate at a constant efficiency over a wide range of temperatures. Drierite® and Anhydrocel® are trade names for commercially available calcium sulfate mixtures, and, as with silica gel, these adsorbents are available in indicating and non-indicating forms. Anhydrous magnesium perchlorate has the best drying efficiency of the compounds named, but it has a certain drawback: explosive compounds may be formed if the regeneration step occurs in the presence of organic vapors. For this reason, hydrocarbons must be removed before regeneration. Anhydrous magnesium perchlorate is also deliquescent; i.e., it will melt when removing moisture from the air.

Absorption

Absorption is another method of drying a gas stream. Absorption, usually with liquid desiccants, is not as efficient as with solid desiccants, but it has a higher drying capacity because the liquid can be constantly recirculating. This process with liquid desiccants takes place in much the same way as in a scrubbing tower: the gas comes into contact with the liquid and the water vapor is absorbed. Strong acids and bases are good liquid desiccants, but they will emit corrosive vapors.

Condensation

Drying gases by condensation (cooling) is an excellent method for some purposes; all that is required is that the gas be cooled below its dew point, thereby removing the water vapor from the gas stream. The process is quite simple; the sample gas enters a vessel and is cooled. When the gas has been cooled below the dew point, the water vapor condenses on the inner walls of the vessel and is removed from the gas stream; e.g., a solution of dry ice and acetone at a temperature of - 78.5°C will remove all but 0.01 mg/liter, and a cooling bath of liquid nitrogen at a temperature of - 196°C will remove all but 1×10^{-23} mg of water vapor/liter of air. Table 4-14 lists various cold bath solutions and their temperatures.

Table 4-14. Summary of cold bath solutions.

Coolant	Temperature, °C
Ice and water [a]	0
Ice and NaCl	- 21
Carbon tetrachloride slush [a. b]	- 22.9
Chlorobenzene slush [a, b]	- 45.2
Chloroform slush [a, b]	- 63.5
Dry ice and acetone [a]	- 78.5
Dry ice and cellosolve [a]	- 78.5
Dry ice and isopropanol [a]	- 78.5
Ethyl acetate slush [a, b]	- 83.6
Toluene slush [b]	- 95
Carbon disulfide slush [a, b]	- 111.6
Methyl cyclohexane slush [a, b]	- 126.3
n - Pentane slush [b]	- 130
Liquid air	- 147
Isopentane slush [b]	- 160.5
Liquid oxygen	- 183
Liquid nitrogen	- 196

Note a: Adequate for secondary temperature standard.

Note b: The slushes may be prepared by placing solvent in a Dewar vessel and adding small increments of liquid nitrogen with rapid stirring until the consistency of a thick milkshake is obtained.

Mechanical refrigeration devices especially designed for water removal are commercially available.

Permeation Membrane (Heatless) Dryers

A *permeation membrane dryer* use a material called Nafion (a copolymer of Telfon and perfuoro-3); selectively permeable membrane tubing to continuously dry gas streams removing only water vapor. These dryers operate over a wide range of temperatures, pressures and flow rates, and dry to dew points as low as -45°C. Permeation dryers operate by transferring moisture from one gas stream to a counter-flowing purge gas stream, much like a shell-and-tube heat exchanger transfers heat. Water molecules permeate through the Nafion tube wall, evaporating into the purge gas stream. The water concentration differential between the two gas streams drives the reaction, quickly drying the air or gas. Purge gas should be dry (-40°C dew point) air or other gas. If no dry gas is available, a portion of the gas dried by the Nafion dryer can act as the purge gas in a split-stream or reflux method.

Summary

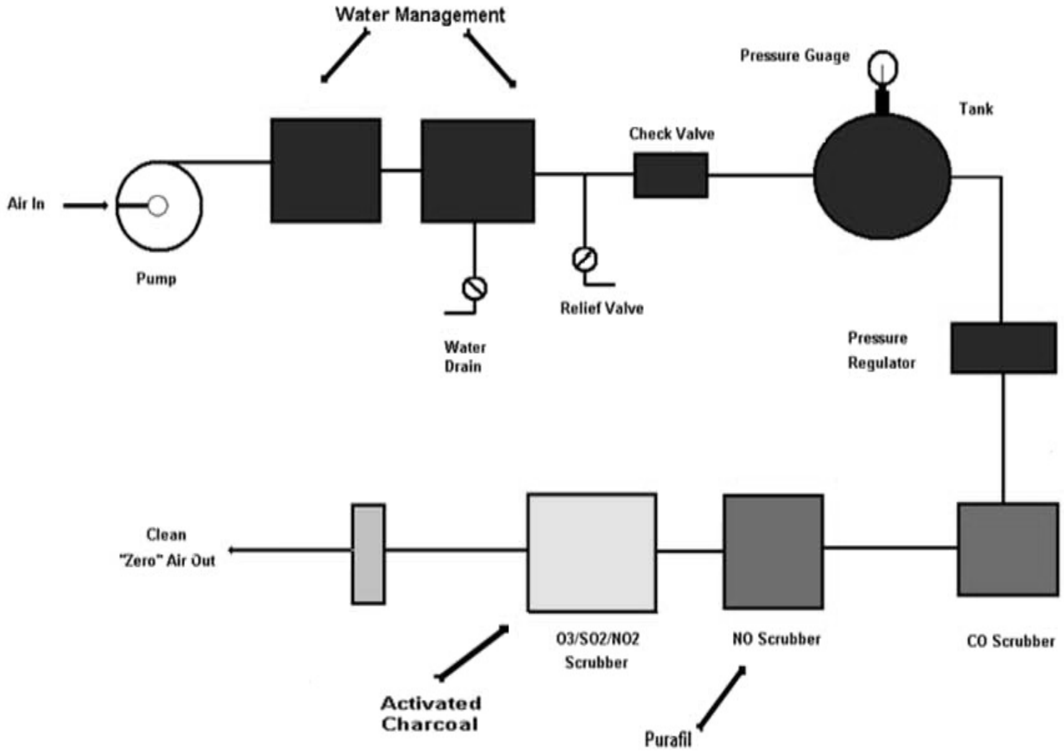
Molecular sieves and activated carbon are used extensively for removal of gaseous contaminants. These solid adsorbents have a porous quality that gives them an extremely high surface area per unit weight, thus increasing their adsorptive capacities.

There are adsorbents and absorbents that will selectively remove one gas from an air stream and leave the others. These include Hopcalite® for selectively removing CO from an air stream, manganese dioxide for removing ozone from an air stream, Ascarite for removing CO_2 from an air stream, and Purafil® for selectively removing NO_2 from an air or NO_x stream.

For the removal of water vapor, there are basically four methods used: condensation, absorption, adsorption and permeation (heatless dryers). Condensation is the most efficient means of drying a gas stream, but may be awkward to use. Absorption, using liquid desiccants, has the greatest capacity for drying a gas stream because the liquid can be recirculated continuously. This method, too, may be awkward for field work. Adsorption of water vapor using solid adsorbents is used extensively because of the ease of handling and storage and the advantage of the regenerative properties. Permeation membrane dryer devices employ a continuous and self-regenerating drying process. It is highly selective, compact, corrosion resistant, and has no moving parts and requires no routine maintenance.

The schematic shown in Figure 4-10 illustrates a typical zero air generator which utilizes many of the gas scrubbing processes and devices discussed in this section.

Figure 4-10. Typical schematic of a zero air generator.



The zero air generator or cylinders should be able to provide air below the stated *lower detection limits* (LDL) of the instruments you are testing. This issue is of particular concern when generating zero air for the calibration of *precursor gas* analyzers since the concentrations of the constituents of interest may be only slightly above the instruments LDL. For example, the LDL for precursor gas analyzers are as follows:

- NO, 50 ppt
- SO_2, 100 ppt
- CO, 40 ppb

Sample Problems

Problem 1

A sample gas stream containing sulfur dioxide is to be scrubbed with an adsorbent while the sample collection is performed. The SO_2 concentration is known to be approximately 10 ppm (10 µl/l). The adsorbent to be used is activated carbon. The sampling rate is 200 l/min to be maintained for 24 hours. How much activated carbon would be needed to remove all of the SO_2 for the entire length of the sampling period?

Solution

The total amount of sampled air can be calculated: 200 l/min x 60 min/hour x 24 hours = 288,000 liters.

The total amount of SO_2 that must be scrubbed from the sample is calculated: 288,000 l of air x 10 µl of SO_2/l of air= 2,880,000 µl of SO_2 to be removed. For the purposes of this example 1 ml = 1 cm^2 (this will actually add very little error). 2.88×10^6 ul SO_2 x 10^{-6} ml/µl x 1 cm^3/ml = 2880 cm^3 of SO_2 to be removed.

From Table 4-8, activated carbon will adsorb 380 cm^3 of SO_2 per gram of adsorbent (assuming adsorption takes place at 15°C).

The total carbon that is necessary can be calculated:

$$\frac{2880\ cm^3 SO_2}{380 \frac{cm^3\ SO_2}{1\ g\ carbon}} = 7.6\ g\ carbon$$

7.6 grams of carbon would be needed to effectively remove the SO_2 from the gas sample. This is an approximate amount.

Problem 2

A sample stream contains approximately 2% (by weight) water vapor, which must be removed. Molecular sieve Type 4A has been chosen as the drying agent. Sampling is to be performed at 2.5 l/min for 8 hours. How much 4A molecular sieve is needed to dry the air for the length of the sample period? (Assume adsorption takes place at 25°C.)

Solution

The total amount of air sampled:

2.5 l/min x 60 min/hour x 8 hours = 1200 liters.

The density of air at 25°C and 1 atm is 1.1844 mg/ml.

The weight of the air sampled:

= 1200 liters x 1000 ml/l x 1.1844 mg/ml = 1,421,300 mg of air sampled.

The weight of water vapor to be removed:

= 1,421,300 mg x 0.001 g/mg x 0.02 = 28.43 g.

From Table 4-11, 4A molecular sieves will remove 24.5 g of H_2O per 100 g of sieve. The amount of sieve necessary to fully dry the air stream (this is an approximate value):

$$\frac{28.43\ g\ H_2O}{24.5\,\frac{cm^3\ H_2O}{100\ g\ sieve}} = 116g\ molecular\ sieve\ Type\ 4A$$

Summary

Standard test atmospheres are very important as calibration sources for atmospheric monitors. The bag-filling method is best suited for "batch" calibration purposes where only a small amount of calibrated gas is needed at one time. For example, a series of known CO concentrations can be made very quickly with this technique. The cylinder method, permeation tube method, and ozone generators are best used where a constant flow of calibration gas is needed. Most continuous atmospheric monitors and all manual sampling trains require this type of calibration technique because of the finite time required to obtain an adequate sample.

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Chapter 5

Sulfur Dioxide Measurement Principles and Calibration Procedures

Introduction

In this chapter, the discussion will begin with the reference and equivalent methods for the measurement of sulfur dioxide (SO_2) in the atmosphere (i.e., measurement principles) and the associated calibration procedures for these methods. Sulfur Dioxide is the only gaseous criteria pollutant for which the reference method is a manual method; requiring separate procedures for sampling and analysis. The equivalent methods for the determination of SO_2 in ambient air are currently the methods of choice since they employ automated continuous instruments.

While the obvious problems of widespread elevated concentrations have been largely solved for some criteria pollutants, problems related to particulate matter (PM), ozone (O_3), and toxic air pollutants remain. It is now clear that even very low air pollution levels can be associated with adverse environmental and human health effects. As a result, the use of highly sensitive commercial air pollutant monitors for the characterization of the precursor gases CO, SO_2, and total reactive oxides of nitrogen (NOy) in a new national core monitoring network (NCore). The high sensitivity CO and SO_2 analyzers are fundamentally the same as those designated as Federal Reference and Equivalent methods (http://www.epa.gov/ttn/amtic/criteria.html), but with Precursor Gas Technical Assistance Document (TAD) modifications to improve sensitivity and accuracy or reduce interferences. The use of such precursor gas analyzers in the NCore network will still allow determination of compliance with the NAAQS, but will provide measurements at much lower detection limits than are achievable by current monitors. The implementation of high sensitivity monitoring for CO, SO_2, and NOy in the NCore network will require installation of new analyzers at selected sites, and implementation of new monitoring, calibration, and data acquisition procedures. The purpose of Precursor Gas TAD is to provide state, local, and tribal (S/L/T) agencies with guidance on the equipment, procedures, data acquisition, and quality assurance/quality control (QA/QC) efforts needed to properly implement high sensitivity precursor gas monitoring.

A discussion of the sampling and analyzer design considerations for precursor gas monitoring will be provided following the discussion on monitoring with the traditional instruments (based on the USEPA's Equivalent methods).

High sensitivity precursor gas analyzers will increasingly be brought online; however, traditional analyzers will remain part of the NAAQS monitoring network for many years to come.

Pararosaniline Method: Reference Method for the Determination of SO_2 in the Atmosphere

The reference method for the determination of sulfur dioxide in ambient air is a wet-chemical colorimetric process involving spectrophotometric analysis. This method is referred to as the West-Gaeke Method or more commonly as the Pararosaniline Method. This is a manual method requiring the sampling of ambient air for later analysis. A brief description of the Reference Method is presented here to provide the reader with a general understanding of manual sampling for gaseous constituents.

In sampling for SO_2, ambient air is drawn through an absorber containing a solution of potassium terachloromercurate (TCM). Any sulfur dioxide present in the ambient air is absorbed in the solution, thereby reacting with the TCM to form a monochlorosulfonatomercurate complex, which is resistant to any further oxidation from strong oxidants which might be present in the air (e.g., ozone, oxides of nitrogen, oxygen). Sampling times are most often 30 minutes, 1 hour, or 24 hours, depending on the results desired, type of sampling, and the expected ambient SO_2 concentrations. Sampling flow rates and subsequent air volumes are dependent on sample time. A typical sampling train used to sample for SO_2 for a 24 hour period is shown in Figure 5-1.

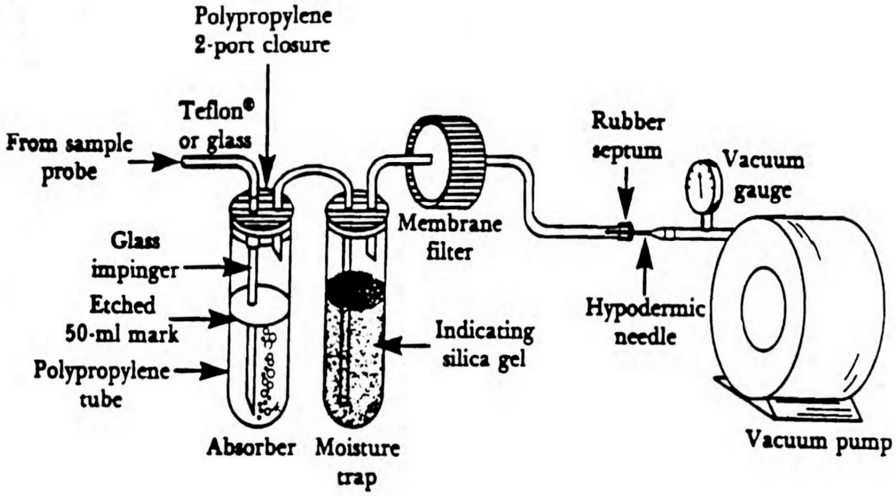

Figure 5-1 Typical 24 hour sampling train

After sampling is completed, the absorbing solution is allowed to set for 20 minutes to allow any ozone in the solution to decompose. The absorbing solution is then treated with sulfamic acid to destroy any nitrite, which results from the absorption of oxides of nitrogen from the sampled atmosphere (Pate et al. 1965). Next, the solution is treated with a 0.2% formaldehyde solution and the pararosaniline. Pararosaniline, formaldehyde, and the bisulfate anion react to form the bright pinkish-colored methyl sulfonic acid. Between 30 and 60 minutes after the addition of pararosaniline, the solution is analyzed spectrophotometrically at 548 nm, and SO_2 concentration is determined from a calibration curve prepared using sodium sulfite-TCM standardized solutions or an SO_2 permeation tube. Additional information regarding the pararosaniline method can be found 40 CFR 50 Appendix A.

The pararosaniline method is rarely used since the advent of continuous, automated instrumental methods for sulfur dioxide with equivalent accuracy and precision of this wet-chemical reference method. Constant on-line monitoring, real-time data output, greater sensitivity, and the ability to transmit data directly into computerized data acquisition systems and/or remote telemetry systems represent major advantages of instrumental techniques.

UV Fluorescence Spectroscopic Instruments

The Ultraviolet (UV) fluorescence monitoring method for atmospheric SO_2 was developed to improve upon the flame photometric detection (FPD) method for SO_2, which in turn had displaced the pararosaniline wet chemical method for SO_2 measurement. The pararosaniline method remains the U.S. EPA's Reference Method for atmospheric SO_2, but is rarely used because of its complexity and slow response, even in its automated forms. Both the UV fluorescence and FPD methods are designated as Equivalent Methods by EPA, but UV fluorescence has largely supplanted the FPD approach because of the UV method's inherent linearity, sensitivity, and the absence of consumables, such as the hydrogen gas needed for the FPD method.

The focus of this chapter will be to discuss the automated UV fluorescence monitoring method as the measurement principle for sulfur dioxide in the atmosphere. Any analyzer that uses the specified measurement principle, meets the prescribed specification, and is calibrated in accordance with the specified calibration procedure may be designated an equivalent method by EPA. The calibration procedure consists of checking the analyzer's response by "challenging" the analyzer with known concentrations of sulfur dioxide.

Detection and Measurement Principle

Fluorescence spectroscopy is the measurement of "fluorescent" light emitted by certain molecules when excited by a radiation source of appropriate energy or wavelength. In this process, the molecule that is excited by the light energy will remain excited for about 10^{-8} to 10^{-4} seconds. This time period will be sufficient for the molecule to dissipate some of this energy in the form of vibrational and rotational motions. Because some of the original light energy is dissipated in this way, the resultant light energy emitted by the molecule is of lower energy than the original light source. Therefore, the "fluorescent" light observed from the molecule is of a longer wavelength (shorter frequency). The wavelengths of light which excite a compound and fluoresce from it are individually characteristic of that compound and can be used to both identify and quantify it.

When using fluorescence spectroscopy for quantitative analysis, emission intensity is dependent on the total number of excited molecules and is, therefore, theoretically directly proportional to concentration. This holds true at very low concentrations; however, as concentration increases, absorption by the sample of both primary and secondary light becomes significant, finally resulting in a phenomenon called "concentration quenching". Quenching is the process which occurs when an excited molecule collides with another molecule before it can release its extra energy as light. The energy is dissipated in the collision and, therefore, the presence of the molecule is not noted by the fluorimeter. Other gases present in a sample can also exhibit varying degrees of quenching. Due to concentration quenching, the linear plot of concentration verses instrumental response may reach a plateau and return toward baseline. When this occurs, dilution of samples is required (APHA).

To assure a measurable difference between the light absorbed and the light fluoresced, a high energy, short wavelength source of light is used in fluorescence spectroscopy instruments. This is best supplied by an ultraviolet (UV) light source.

Chemistry

Fluorescence spectroscopy has been applied to ambient air monitoring for sulfur dioxide. Sulfur dioxide absorbs light in three primary regions:

Region	**Wavelength**
1	390 nm to 340 nm
2	320 nm to 250 nm
3	230 nm to 190 nm

Regions 1 and 2 tend to exhibit high degrees of quenching with other molecules found in ambient air and are, therefore, not suited to SO_2 monitoring applications. Region 3 is free of quenching by air and most other molecules that would be found in ambient air. It is for this reason that the excitation energy for SO_2 fluorescence comes from Region 3.

Ultraviolet radiation in Region 3 is used to irradiate the sample gas containing SO_2. The high energy ultraviolet light is absorbed by SO_2 and excites it to SO_2^* by Equation 5-1:

(Eq. 5-1) $$\mathrm{SO_2} + h\nu_1 \xrightarrow{\mathrm{I_a}} \mathrm{SO_2}\,*$$

The ultraviolet light in the system is given by Equations 5-2:

(Eq. 5-2) $$\mathrm{I_a} = \mathrm{I_o}\left[1 - \mathrm{Exp}(-a\ell[\mathrm{SO_2}])\right]$$

Where: I_a= irradiating light (ultraviolet)
I_o = incident light intensity
a = absorption coefficient of SO_2
ℓ = length of light path through sample
$[SO_2]$= sulfur dioxide concentration

The excited SO_2* can then return to the ground state by fluorescence:

(Eq. 5-3) $$\mathrm{SO_2}* \xrightarrow{\mathrm{K_f}} \mathrm{SO_2} + h\nu_2$$

Or by quenching:

(Eq. 5-4)
$$SO_2{*} + M \xrightarrow{K_q} SO_2 + M$$

where M is the quenching species characteristic of the background air or by dissociation by Equation 5-5:

(Eq. 5-5)
$$SO_2{*} \xrightarrow{K_d} SO + O$$

Using the above equations, an expression can be written representing the fluorescent intensity, available at the detector, from this process:

(Eq. 5-6)
$$I_f = \frac{K_f I_o \left[1 - \mathrm{Exp}(-a\ell[SO_2])\right]}{K_f + K_d + K_q[M]}$$

Where: I_f = intensity of the fluorescence
I_o = incident light intensity
a = absorption coefficient of SO_2
ℓ = length of light path through sample
$[SO_2]$ = sulfur dioxide concentration
K_f = rate constant, fluorescence
K_q = rate constant, quenching
K_d = rate constant, dissociation
$[M]$ = concentration of quenching molecules

When the SO_2 concentration is relatively low and the path length of exciting light (ultraviolet) is short, the above expression reduces to:

(Eq. 5-7)
$$I_f = \frac{K_f I_o a\ell[SO_2]}{K_f + K_d + K_q[M]}$$

and since K_f, K_d, K_q, $[M]$, I_o, and ℓ are constant, then:

(Eq. 5-8)
$$I_f \alpha [SO_2]$$

the fluorescent signal (I_f) is directly proportional to the SO_2 concentration (Wolfe and Oliver 1975) (Zolner, Cieplinski, and Helm).

Apparatus

Typically, the fluorescent SO_2 analyzer can be conveniently divided into two major components: the analyzer and the electronics. The TECO 43 series analyzer serves the purpose for the following demonstration of a basic fluorescent analyzer. Figure 5-2 is a basic diagram of an SO_2 fluorescence analyzer. Sample gas enters the analyzer via a diaphragm pump and is directed through hydrocarbon "kicker," which removes hydrocarbons from the sample by forcing the hydrocarbon molecules to permeate through the tube wall. The SO_2 molecules pass through the hydrocarbon "kicker" unaffected. The sample flows into the fluorescence chamber, where pulsating UV light excites the SO_2 molecules. The condensing lens focuses the pulsating UV light into the mirror assembly. The mirror assembly contains four selective mirrors that reflect only the wavelengths which excite SO_2 molecules. As the excited SO_2 molecules decay to lower energy states they emit UV light that is proportional to the SO_2 concentration. The bandpass filter allows only the wavelengths emitted by the excited SO_2 molecules to reach the photomultiplier tube (PMT). The PMT detects the UV light emission from the decaying SO_2 molecules. The photodetector, located at the back of the fluorescence chamber, continuously monitors the pulsating UV light source and is connected to a circuit that compensates for fluctuations in the UV light. The sample, upon exiting the fluorescence chamber, flows through a flow sensor, a capillary, and the shell side of the hydrocarbon "kicker."

The "Kicker" assembly consists of the membrane tube and Teflon tube. The pump creates the vacuum between the membrane and the Teflon tube causing a differential pressure. Poly-nuclear Hydrocarbon (PAH) in the sample is removed while passing through membrane tube by this differential pressure.

The electronics section can be further subdivided into two main areas of interest: the ultraviolet light source, and the signal processing electronics. Early in the development of SO_2 fluorescence analyzers it was recognized that a long lived, compact, high energy UV light source would be required before the instrument would be practical for air monitoring. After considerable investigation, it was determined that a pulsed source of ultraviolet light would satisfy the requirements of high irradiation energy, long life, and small size. The original fluorescence analyzer manufactured by the Thermo Electron Corporation was termed a "pulsed-phased fluorescence SO_2 analyzer" due to the use off the pulsed source of light. Newer model fluorescence SO_2 analyzers (Beckman, Monitor Labs) use a continuous source of ultraviolet light. The light from the source is filtered by a bandpass filter to assure that the light entering the fluorescence chamber is 210 nm (remember Region 3) which allows the most advantageous excitation of sulfur dioxide molecules. Another filter (350-nm bandpass) is used on light exiting the chamber to eliminate interference which can occur within the range of the fluorescence emission spectrum.

The signal processing section is composed of a preamplifier which converts the photovoltaic tube current pulses to voltage pulses. The amplifier then increases the voltage signals to useable levels. The signal is then filtered and routed to a meter display/recorder circuit.

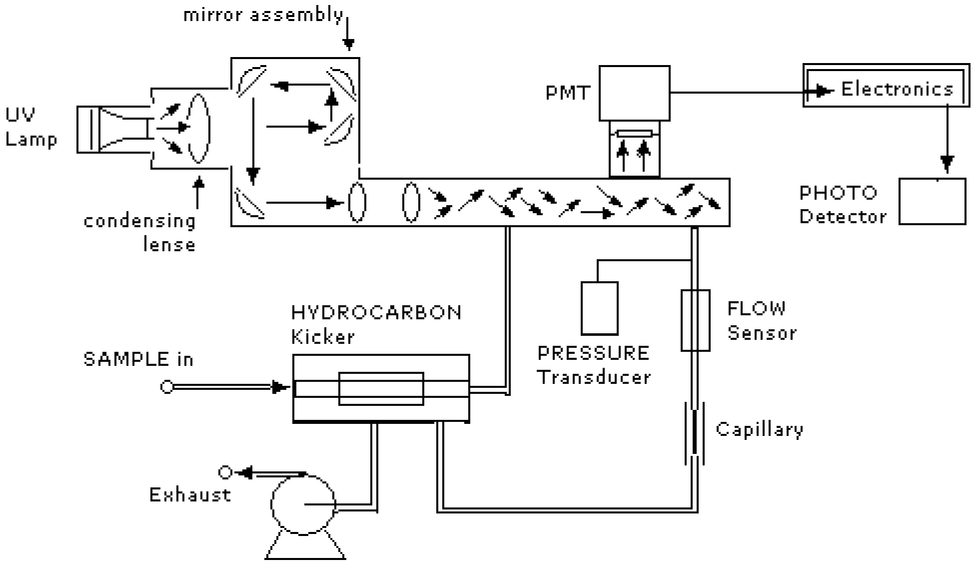

Figure 5-2. Fluorescence SO_2 analyzer. (Source: TECO Model 43C Operating Manual)

Calibration

Calibration of the instrument may be achieved by two methods: a permeation tube system or a dynamic dilution system connected to a cylinder of standardized gas. The permeation method uses the same equipment and setup as shown in Chapter 4 - *Generation of Test Atmospheres.* At least four concentrations of sulfur dioxide within the working range of 10 to 95% full scale and zero air are introduced to the analyzer. The instrument's response is compared to the standards introduced, and the instrument is adjusted to give accurate readings. Frequent (once a day) zero and single point calibration checks (80% full scale) are prudent after the instrument is placed in service. Calibration should be carried out under the same conditions as are found when analyzing ambient concentrations. Refer to the instrument's operation manual for more detailed and specific calibration procedures.

Calculations

Carbon monoxide analyzers generally read out directly in ppm. Before the direct concentration readout is utilized, it is necessary to calibrate the analyzer using known concentrations of gases. If it is necessary to convert CO concentrations from ppm to milligrams per cubic meter (mg/m^3), the following conversion factor can be used:

(Eq. 5-9) $$\frac{\text{mg}\,SO_2}{\text{m}^3} = \text{ppm}\,SO_2 \times 2.61$$

If the analyzer does not readout in ppm, but rather in $\frac{\text{mg SO}_2}{\text{m}^3}$, the following factor can be used to derive the ppm SO_2 concentration:

(Eq. 5-10)
$$\text{ppm SO}_2 = \frac{\text{mg SO}_2}{\text{m}^3} \times 0.388$$

Calibration Procedure

Calibration consists of determining the response of the instrument to various known concentrations of sulfur dioxide generated and preparing calibration curves or tables. Calibration of the instrument may be achieved by two methods: a permeation tube system or a dynamic dilution system connected to a cylinder of standardized gas. Refer to Chapter 4 - *Generation of Test Atmospheres*, for further details regarding dynamic dilution and/or permeation techniques to generate calibration standards. The analyzer is set up in its sampling mode and "zero" gas is introduced via the analyzer's sampling line. The zero adjustment control is set to give an instrument readout reflecting zero concentration. An SO_2-free (< 0.0005 ppm) air supply is required for the proper calibration and evaluation of the analyzer. There are several methods that are acceptable to generate this zero gas (Chapter 4 - *Generation of Test Atmospheres*).

The next step in calibration is the introduction of the span gas. This gas should have a SO_2 concentration that is approximately 80% of the instrument's operating range (e.g., 80% of an upper range limit – URL, value of 0.500 ppm is 0.400 ppm). The instrument's span adjustment control is set so that the instrument's output reflects the span gas concentration. At least three other concentrations of sulfur dioxide covering the analyzer's operating range are then introduced to check linearity of response. SO_2 cylinder gases may consist of SO_2 and dry nitrogen if they are to be diluted to at least 100:1 with air when preparing calibration gases. The nominal concentration for a cylinder of SO_2 is 50 ppm. Standard Reference Materials (SRMs) or gaseous standards traceable to SRMs are required for calibrating and auditing ambient air and stationary source pollutant monitoring systems. Refer to the document, EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards, for further details regarding EPA Standard Reference Materials (SRMs). If a data recorder is used with the analyzer, it should be adjusted to reflect the calibration standards. A calibration curve should be prepared for each instrument calibration. The instrument's operating manual should be consulted for additional recommendations concerning calibration.

Frequent (once a day) zero and single point calibration checks (80% full scale) are prudent after the instrument is placed in service. Calibration should be carried out under the same conditions as are found when analyzing ambient concentrations.

Method Characteristics and Capabilities

Advantages

These instruments are well suited to ambient air monitoring in that they have a fairly rapid response time, require no ancillary equipment or reagents, and are relatively insensitive to changes in temperature and flow variations. Fluorescence SO_2 monitors have proven to be reliable and maintenance free for extended periods. Unlike flame photometric analyzers, they are capable of being located in areas where flammable gases would cause a hazard.

Interferences

The principle interferences to the fluorescence technique include water vapor, oxygen, and aromatic hydrocarbons. Water vapor and oxygen act as interferences in that they quench the fluorescence emissions resulting in the instrument reporting a lower than true SO_2 concentration. Interference by water can be alleviated using a drying element on the sample gas. Some manufacturers utilize a permeation dryer (e.g. Nafion dryer) to removes vapor phase moisture (which results in quenching) from the gas stream while leaving the SO_2 molecules unaffected. The dry gas then enters the fluorescence chamber. After the sample air exits the chamber it passes over the outside of the permeation dryer; regaining the moisture removed, and is then passed to the outside air unaltered, thereby keeping it continuously regenerated. More commonly in modern SO_2 instruments, water interference is minimized by selection of the incident wavelength used for measurement.

The effect of oxygen quenching can be minimized by maintaining identical oxygen concentrations in the calibration gases as found in the air sampled.

Certain aromatic hydrocarbons will fluoresce at the same wavelength band as SO_2, thereby giving high results. The most significant of these is a class of hydrocarbons called polynuclear aromatic hydrocarbons (PAH); of which naphthalene is a prominent example. Xylene is another hydrocarbon that can cause interference. These hydrocarbons can be eliminated from the sample gas by use of hydrocarbon "kicker" upstream of the reaction chamber. These devices operate on a selective permeation principle, allowing only hydrocarbon molecules to pass through the tube wall, while allowing SO_2 molecules to pass through unaffected. The driving force for the hydrocarbon removal is the differential partial pressure across the wall. This differential pressure is produced within the instrument by passing the sample gas through a capillary tube to reduce its pressure and feeding it into the shell side of the hydrocarbon kicker. These devices are non-serviceable. If malfunction is suspected a leak check should be performed based on manufacturer's instructions and the device replaced if it fails the test.

Nitrogen oxide (NO) also fluoresces in a spectral range close to SO_2. Interference from NO is addressed by the presence of the band pass filter, which allows only the wavelengths emitted by the excited SO molecules to reach the PMT.

Range and Sensitivity

Fluorescence SO_2 monitors have a potential range of 0.2 to 250 mg/m^3 (0.050 ppm to 100.0 ppm).

Problems, Precautions, Troubleshooting

Fluorescence SO_2 monitors are characteristically dependable, low-maintenance instruments. Some areas where problems do arise are the following:

As mentioned in the section on flame photometric SO_2 analyzers, the photomultiplier tube can degrade and periodically needs replacing. Again, if the pmt is replaced, then "burning in" of the pmt is necessary before the instrument is brought on line again.

A lowering of response in a fluorescence analyzer may indicate that the ultraviolet light source needs replacing. This can be determined by injecting a low level known concentration SO_2 gas and noting if the response is lower than normal. Another cause of lowered response is increased quenching due to moisture or dirt in the fluorescence chamber. This can be alleviated by cleaning the chamber (see instructions in the analyzer's operating manual) and then replacing the permeation dryer, if so equipped. Ensure that an appropriate filter is in place at the sample inlet. The instrument's automated diagnostic system and the operating manual are the best source for aids in troubleshooting and maintenance.

Prior to undertaking extensive troubleshooting procedures, realize that many instrument malfunctions are related to system or subsystem flow leaks.

Quality Assurance

Quality assurance is in important consideration of monitoring. The requirements of a QA program for all types of reference and equivalent methods are contained in the following:

Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II: Part 1
Ambient Air Quality Monitoring Program Quality System Development, EPA-454/R-98-004, August 1998.

High Sensitivity SO_2 Analyzer – Percursor Gas Monitoring

Since the high sensitivity SO_2 analyzers deployed at NCore sites are intended to monitor low ambient SO_2 concentrations, it is important that they meet a variety of performance criteria. Many of these performance criteria are more stringent than those for routine SO_2 analyzers; consequently, a number of features are required in the high sensitivity SO_2 analyzers in order to achieve the performance criteria.

The following section describes the recommended performance criteria and the analyzer features that are recommended in order to achieve the performance criteria at the NCore sites.

Recommended Method Performance Criteria

The U.S. EPA has recently assessed the measurement quality objectives needed for high sensitivity precursor gas monitoring in NCore, relative to the long-established statistics stated in 40 CFR 58. In particular, EPA recommends that measurement quality objectives for bias and precision be based on upper confidence limits at the monitoring site level, to provide a higher probability of reaching appropriate conclusions (e.g., in comparisons to NAAQS). The intent of this recommendation is to move S/L/T agencies to a performance-based quality system i.e., allowing organizations that show tight control of precision and bias to reduce the frequency of certain QC checks, and to focus their quality system efforts where most needed.

The U.S. EPA recommends that the high sensitivity SO_2 analyzers that are deployed at NCore sites meet the following method performance criteria. Additional details regarding these criteria can be found in USEPA Technical Assistance Document (TAD) For Precursor Gas Measurements in the NCore Multi-Pollutant Monitoring Network, Version 4, (EPA-454/R-05-003).

Precision

Precision is defined as the measure of agreement among individual measurements of the same property taken under the same conditions. Precision is assessed from checks that are performed at least once every two weeks and should be used to assess precision on a quarterly basis. It is recommended that high sensitivity SO_2 analyzers have a 95 percent probability limit for precision of ±15 percent or less. Calculation of precision starts with the comparison of the known challenge concentration used in the precision checks to the corresponding measured concentrations reported by the analyzer.

Bias

Bias is defined as a systematic or persistent distortion of a measurement process that causes errors in one direction. Bias is assessed from the degree of agreement between a measured value and the true, expected, or accepted value. Analyzer bias is calculated using comparisons of known challenge concentrations to the corresponding measured concentrations reported by the analyzer. The challenge comparisons used to assess bias should be the same as those used to assess precision. It is recommended that high sensitivity SO_2 analyzers have an upper bound for the average bias of ± 15 percent or less.

Representativeness

Representativeness refers to whether the data collected accurately reflect the conditions being measured. It is the data quality indicator most difficult to quantify. Unless the samples are truly representative, the other indicators are meaningless. Representativeness for monitoring of low ambient levels of SO_2 in NCore is different than for routine monitoring, since the objectives of the monitoring are much different. Representativeness can only be assured in terms of the appropriate selection of the sampling site, proper implementation of ambient air sampling, and reasonable coverage of the sampling schedule (i.e., 24 hours per day, 7 days per week, ideally).

Completeness

Completeness is defined as the amount of data collected relative to the total expected amount. Ideally, 100 percent of the expected amount of data would always be collected; in practice, completeness will be less for many reasons, ranging from calibration time and site relocation to power outages and equipment failure. For monitoring of ambient SO_2 concentrations in NCore, EPA requires a minimum data completeness of 75 percent. In practice typical completeness values can often approach 90 to 95 percent.

Comparability

Comparability is defined as the process of collecting data under conditions that are consistent with those used for other data sets of the same pollutant. The goal is to ensure that instruments purchased and operated by different states and local agencies produce comparable data. To promote comparability, the USEPA Technical Assistance Document (TAD) For Precursor Gas Measurements in the NCore Multi-Pollutant Monitoring Network, Version 4, (EPA-454/R-05-003) describes the recommended characteristics of high sensitivity SO_2 analyzers and the procedures for their installation and use.

Method Detection Limit

The *method detection limit* (MDL) refers to the lowest concentration of a substance that can be reliably determined by a given procedure. The MDL is typically not provided by the vendor. Based on the objectives of the Precursor Gas Program, it is expected that most sites will be measuring pollutant concentrations at lower ranges than the typical SLAMS/NAMS network. Therefore, the ability to quantify concentrations at these lower levels will be very important. The use of a vendors advertised LDL is sufficient to make intelligent purchasing decisions; however, vendors quantify LDLs under ideal conditions and therefore one might consider this value as the best possible detection that can be achieved.

As these monitors are deployed into monitoring networks, where both environmental conditions, equipment (calibration, dilution devices, sampling lines, gaseous standards) and operator activities can vary, it is important to estimate what pollutant concentrations can truly be detected, above background noise (the potential conditions mentioned above). The site specific MDL establishes an estimate based on the routine operation (and conditions) of that instrument in the network and provides a more meaningful evaluation of data as it is aggregated across the precursor gas network.

It is recommended the MDL for high sensitivity SO_2 analyzers be established prior to putting the analyzers into service, and should be 0.0003 ppm (0.30 ppb) or lower over an averaging time of no more than 5 minutes.

Lower Detectable Limit

The *Lower Detectable Limit* (*LDL)* is the minimum pollutant concentration that produces a signal of twice the noise level. To estimate the LDL, zero air is sampled and the noise level of the SO_2 readings is determined according to 40 CFR 53.23(b). The vendor-specified LDL for the most sensitive range of high sensitivity CO analyzers should be 0.0002 ppm (0.20 ppb) or lower, over an averaging time of no more than 5 minutes.

Linear Range

The *linear range* of each high sensitivity SO_2 analyzer should extend from approximately 0.20 ppb to at least 100 ppb. Users should determine if their range should exceed 100 ppb and adjust accordingly. Note that some high sensitivity SO_2 analyzers can operate simultaneously on a number of ranges, with each range recorded on a separate data logger channel with its own calibration curve. Although requiring slightly more effort to calibrate and maintain, recording of multiple ranges would allow capture of a wide range of SO_2 concentrations.

Zero/Span Drift

Zero drift is defined as the change in response to zero pollutant concentration, over 12- and 24-hour periods of continuous unadjusted operation. Span drift is defined as the percent change in response to an upscale pollutant concentration over a 24-hour period of continuous unadjusted operation. Zero and span drift specifications should be obtained from the vendor prior to putting a high sensitivity SO_2 analyzer into service. Such SO_2 analyzers should have 12- and 24-hour zero drift less than 0.20 ppb, and should have a span drift of less than ±1 percent of the full scale measurement range of the analyzer per 24 hours.

NO Rejection Ratio

The NO rejection ratio refers to the effectiveness with which fluorescent emission from nitric oxide (NO) is blocked in a UV fluorescence SO_2 analyzer. This interfering emission can be greatly reduced by optical filtering of the light reaching the PMT. For high sensitivity SO_2 monitoring in NCore, it is recommended that the NO rejection ratio of the SO_2 analyzer be at least 100 to 1, i.e., 100 ppb of NO must produce a response equivalent to that from no more than 1 ppb of SO_2.

Recommended Features for High Sensitivity SO_2 Measurements

Continuous UV fluorescence SO_2 analyzers are commercially available from a number of vendors. The design of these analyzers is similar among vendors with some slight variations. A schematic diagram of a typical high-sensitivity fluorescence instrument is essentially the same as that of a traditional or routine fluorescence instrument (Figure 5-2). In general, analyzers contain the following systems:

1. *Pneumatic System*: This portion of the analyzer consists of sample probe, sample inlet line, particulate filter, hydrocarbon scrubber/kicker, dryer (if needed), sample cell, flow meter, and pump, all used to bring ambient air from the inlet to the detector.
2. *Analytical System*: This portion of the analyzer consists of the UV source with the associated source filters, lenses, and optics, as well as the light baffles, the detector (photomultiplier tube), and bandpass filters.
3. *Electronic Hardware*: This portion of the analyzer consists of the electronic components that control the analyzer and process the signals. This part of the analyzer generally requires little or no maintenance. If the instrument is operated outside the manufacturer's recommended temperature range, however, individual integrated chips can fail and cause problems with operation, data storage, or retrieval.

In addition to these general systems, the high sensitivity versions of the commercial

UV fluorescence SO_2 analyzers typically have the following features that allow them to measure SO_2 at sub-ppb levels:

1. A high intensity pulsed UV light source that provides a greater degree of sensitivity;
2. Multiple reflective optical filters that allow only light at the wavelength causing excitation of the SO_2 molecules to enter the optical chamber, while excluding all light at wavelengths that may cause interference; and,
3. Optical filtering to maximize the rejection of fluorescence from NO molecules.

It is recommended that the high sensitivity SO_2 analyzers deployed in NCore employ these features.

Potential Problems and Solutions

This section describes several of the potential problems associated with precursor SO_2 measurements, and discusses the practical solutions to these problems, many of which the SO_2 analyzer vendors have already implemented in their analyzers.

The following sections describe several potential positive and negative sources of interference or bias. In each section recommended procedures to minimize these interferences or sources of bias are described.

Sources of Positive Interference or Bias

Positive interference in precursor SO_2 monitoring can result from other gases in the sample that happen to fluoresce at the same wavelength as SO_2. Perhaps the most prevalent sources of this type of interference are volatile aromatic (e.g., xylenes) and poly-nuclear aromatic (PNA) (e.g., naphthalene) hydrocarbons. Such compounds absorb UV photons and fluoresce in the region of the SO_2 fluorescence. Consequently, any such aromatic hydrocarbons that are in the optical chamber can act as a positive interference. To remove this source of interference, the high sensitivity SO_2 analyzers have hydrocarbon scrubbers or “kickers” to remove these compounds from the sample stream before the sample air enters the optical chamber, as discussed earlier in this chapter regarding traditional, routine analyzers.

Another potential source of positive interference is nitric oxide (NO). NO fluoresces in a spectral region that is close to the SO_2 fluorescence. However, in high sensitivity SO_2 analyzers, the bandpass filter in front of the PMT is designed to prevent NO fluorescence from reaching the PMT and being detected.

Care must be exercised when using multi-component calibration gases containing both NO and SO_2 that the NO rejection ratio of the SO_2 analyzer is sufficient to prevent NO interference.

The most common source of positive bias (as opposed to positive spectral interference) in high sensitivity SO_2 monitoring is stray light reaching the optical chamber. Since SO_2 can be excited by a broad range of UV wavelengths, any stray light with an appropriate wavelength that enters the optical chamber can excite SO_2 in the sample and increase the fluorescence signal. Furthermore, stray light at the wavelength of the SO_2 fluorescence that enters the optical chamber may impinge on the PMT and increase the fluorescence signal. The analyzer manufacturers incorporate several design features to minimize the stray light that enters the chamber. These features include the use of light filters, dark surfaces, and opaque tubing to prevent light from entering the chamber.

Sources of Negative Interference or Bias

Non-radiative deactivation (quenching) of excited SO_2 molecules can occur from collisions with common molecules in air, including nitrogen, oxygen, and water. During collisional quenching, the excited SO_2 molecule transfers energy kinetically allowing the SO_2 molecule to return to the original lower energy state without emitting a photon. Collisional quenching results in a decrease in the SO_2 fluorescence and results in the underestimation of SO_2 concentration in the air sample.

The concentrations of nitrogen and oxygen are constant in the ambient air, so quenching from those species at a surface site is also constant, but the water vapor content of air can vary. Despite this variability, in routine ambient monitoring the effect of water vapor on SO_2 fluorescence measurements is negligible. Only if high or highly variable water vapor concentrations were a concern (as in source sampling), should it be necessary to dry the sample air using optional equipment available from the analyzer vendors.

Condensation of water vapor in sampling lines must be avoided, as it can absorb SO_2 from the sample air. The simplest approach to avoid condensation is to heat sampling lines to a temperature above the expected dew point, and within a few degrees of the controlled optical bench temperature. An alternative approach would be to maintain all sampling lines at reduced pressure by locating the analyzer's critical orifice at the sample inlet point.

The positive and negative interferences discussed here, in many cases, are common to both the high sensitivity and traditional routine analyzers; however, as a percentage of the measured SO_2 concentration their influence is much greater for the high sensitivity analyzer.

Calibration Equipment

The equipment required for calibration of a high sensitivity SO_2 analyzer includes a MFC calibrator unit, and a source of zero air. The following equipment is recommended for calibration of a high sensitivity SO_2 analyzer.

Calibration Standard and Standard Delivery System

The calibration standards used for the calibration of high sensitivity SO_2 analyzers should be generated by dilution of a commercially-prepared and certified compressed gas SO_2 standard using a MFC calibration unit. That commercially-prepared standard may contain only SO_2 in an inert gas (e.g., N2), or may be a mixed component standard that also contains known concentrations of other precursor ambient gases (e.g., CO, NO). However, note the caution regarding potential NO interference in mixed standards containing SO_2 and NO mentioned previously.

It is important when purchasing a MFC calibrator that it meets the 40 CFR 50 requirements of ±2 percent accuracy, and that the flow rates of both MFC channels are calibrated using a NIST traceable flow standard.

When the analyte concentration in the commercially-prepared standard cylinder is certified by reference to NIST standards, and the MFCs are calibrated to NIST-traceable standards, the resulting working gas concentration is considered to be NIST-traceable.

Refer to Chapter 4 - *Generation of Test Atmospheres*, for more detail regarding the MFC dynamic calibration units and the traceability of calibration standards.

Zero Air Source/Generator

Zero air is required for the calibration of precursor SO_2 instruments. This air must contain no detectable SO_2 (i.e., SO_2 content must be less than the LDL of the SO_2 analyzer) and be free of particulate matter. Suitable zero air may be supplied from compressed gas cylinders of purified air. However, it may be expensive to maintain a sufficient supply of zero air cylinders to operate a precursor SO_2 analyzer continuously. As an alternative, many commercially available zero air generation systems can supply suitably SO_2-free air.

To ensure that the zero air used is free from contaminants, the SO_2 analyzer should be independently supplied with zero air from different sources. If the analyzer responds differently to the different sources, generally the source with the lowest response is the highest quality source. Confirmation of zero air quality can be achieved using various additional scrubbing traps. For example, ambient air can be scrubbed of SO_2 using a 24 x 7 purged activated carbon. The carbon type used for scrubbing is important; Barnebey & Sutcliffe Corp. (formerly Barnebey-Cheney, Columbus, Ohio, www.bscarbon.com), type GI, has been shown to work well.

As an alternative to using an activated carbon scrubber, a sodium carbonate coated denuder, such as the Sunset Laboratory Model #DN-315 stainless steel concentric denuder, can be used.

Alternatively, a cartridge of soda lime attached to the outlet of the zero air system will last for extended periods (potentially over one year) and maintain SO_2 at less than 0.05 ppb.

> *Note: For zero-air sources based on removing SO_2 by means of soda lime, charcoal, or a denuder as described above, the inlet air must be outside ambient air rather than instrument shelter air. Contaminant levels inside the shelter may greatly exceed those in outside air. Also to the extent possible, the components of the zero-air system should be free of materials that might outgas hydrocarbons.*

Reagents and Standards

Routine operation of high sensitivity SO_2 analyzers requires the use of calibration standards and zero air to conduct periodic calibrations and instrument checks. This section describes the requirements for these gases.

Calibration Standards

The primary SO_2 standards used must be certified, commercially-prepared compressed gas standards, with a certified accuracy of no worse than ±2 percent. SO_2 gas standards of 10 to 20 ppm are conveniently diluted with a MFC calibrator down to working concentrations of 20 ppb or less. The commercially-prepared standard may contain only SO_2 in an inert gas (e.g., N_2), or may be a mixed component standard that also contains known concentrations of other precursor ambient gases (e.g., CO, NO). The potential for NO interference must be kept in mind if a standard containing both SO_2 and NO is used for SO_2calibration. It is critical when placing an SO_2 gas standard into service that the cylinder regulator be fully purged to avoid the effect of trace moisture on the delivered SO_2 concentration.

Evacuating the regulator by means of a vacuum line attached to the regulator outlet, before purging for a few minutes with the cylinder gas, is an effective procedure to dry and condition the regulator.

Every gas standard used in precursor gas monitoring must be accompanied by a certificate of calibration from the vendor stating the concentration of the standard, the uncertainty of that certification, and the expiration date of the certification. Standards traceable to NIST are preferred. Certification documents for all standards must be retained in a common location and reviewed periodically so that standards for which the vendor's certification has expired may be removed from service and replaced.

Zero Air

Zero air used as dilution gas for calibration purposes should have an SO_2 concentration below the LDL of the SO_2 analyzer. Multiple zero air sources should be checked, and soda lime, charcoal, or sodium carbonate scrubbers may be necessary to achieve adequate zero air quality. A canister of soda lime followed by a particle filter on the outlet of the zero air source will remove SO_2 for extended periods. Breakthrough can be tested by temporarily adding a carbonate denuder and observing zero gas readings.

Quality Control

A through quality control program is critical to the collection of high sensitivity SO_2 monitoring data and must be implemented at each NCore site. Components of such a program are described below.

Site Visit Checklists and Remote Diagnostic Checks

To determine whether the SO_2 analyzer is working properly, field operators should conduct routine checks of instrument diagnostics and performance every time they visit the monitoring station. Each agency needs to develop diagnostic or maintenance checklists or electronic spreadsheets to document that all required checks have been made. Such lists and sheets should be useful both for collecting diagnostic information and for assessing the quality of the monitoring data. To the extent possible, diagnostic checks can be done remotely, provided the data acquisition system allows remote access to instrument diagnostic information.

Multipoint Calibrations

A multipoint calibration includes a minimum of four points (three spaced over the expected range and a zero point), generated by the calibration system. Although more points may be preferable, current high sensitivity SO_2 analyzers provide inherently linear response over their entire operating range; therefore, four points should be sufficient. Multipoint calibrations must be done prior to the precursor SO_2 analyzer being put into service and at least every six months thereafter. An analyzer should be calibrated (or recalibrated) if any of the following conditions occur:

1. Upon initial installation;
2. The Level 1 span check or precision check difference exceeds 15 percent;
3. After repairs or service is conducted that may affect the calibration;
4. Following physical relocation or an interruption in operation of more than a few days;
5. Upon any indication that the analyzer has malfunctioned or a there has been a change in calibration; or,
6. The measured concentration values during challenges with performance test (audit) samples differ from the certified standard values by ±15 percent. (Generally this challenge is conducted as a blind audit, such that the site operator is not aware of the gas standard concentrations delivered to the analyzers.)

The analyzers should be calibrated *in-situ* without disturbing the normal sampling inlet system to the degree possible.

Level 1 Zero/Span Checks

Level 1 zero and span calibrations are simplified, two-point calibrations used when adjustments may be made to the analyzer. When no adjustments are made to the analyzer, the Level 1 calibration may also be called a zero/span "check" and must not be confused with a level 2 zero and span check. Level 1 zero and span checks should be conducted nightly if the calibration system and SO_2 analyzers used can be programmed to automatically perform these. They are used to assess if the analyzers are operating properly and to assess if any drift in instrument response has occurred.

The zero/span calibrations are conducted by challenging the analyzer with zero air and a test atmosphere containing SO_2 at a concentration of between 70 percent and 90 percent of the full measurement range in which the analyzer is operating. The challenge gas should be sampled through as much of the sampling inlet system as practical to mimic the actual sampling of ambient air.

The results of the Level 1 zero/span check should be plotted on control charts to graphically illustrate the trends in the response of the analyzer to the challenge gases. The span check should not exceed ±15 percent and the zero drift should not exceed ±0.5 percent of full scale. If the measured concentrations fall outside of the control limits, the accuracy of the MFC calibration system should be checked with a NIST-traceable flow standard. If the MFC flow accuracy is confirmed, the data recorded since the last successful Level 1 check should be flagged and the analyzer should be recalibrated using the multipoint calibration procedures as described earlier in this section; in conjunction with the procedures in the instrument's operating manual.

State-of-the-art calibration equipment now exists that is fully automated. These "new generation" calibration units are fully integrated with computers, mass flow calibrators, and the associated hardware and software where they can create test atmospheres manually or automatically. For the precursor gas program, it is recommended that the NCore sites have fully automated calibration capability. Below are a number of reasons why this is advantageous:

- By performing the calibrations or checks automatically, agencies no longer spend the manpower needed to perform them.
- Automated calibrations or checks can be triggered internally or by a DAS. Since newer DASs allow remote access; this allows a remote user to challenge the analyzers without actually being present.
- High sensitivity precursor gas analyzers are expected to have more zero and span drift than less sensitive analyzers; therefore, it is important that a zero and Level I check be performed daily.
- New generation DASs can record calibration data and allow remote users to track daily Level I check and zero drift. This is important for data validation, verification and troubleshooting.

Precision Checks

At least once every two weeks a precision check should be conducted by challenging the SO_2 analyzer with a known low SO_2 concentration to assess the performance of the analyzer. The precision checks should be conducted by challenging the SO_2 analyzer with a standard gas of known concentration between 10 and 50 ppb. After completion of the precision check, the operator should calculate the percent difference between the measured value and the known standard value. Precision should be calculated quarterly, using the calculated percent differences from the precision checks (For more detail on calculating precision, refer to Technical Assistance Document (TAD) for Precursor Gas Measurements in the NCore Multi-pollutant Monitoring Network Version 4, EPA-454/R-05-003). For acceptable precision to be maintained it is recommended that the calibration system's gas flows be verified frequently against a NIST flow standard, and adjusted if necessary before making any adjustments to the analyzer.

Preventive Maintenance and Troubleshooting

Long-term operation of continuous high sensitivity precursor gas analyzers requires a preventive maintenance program to avoid instrument down-time and data loss. This section briefly describes several key items that might be included in the preventive maintenance program established for high sensitivity SO_2 analyzers deployed at NCore sites, as well as some of the troubleshooting activities that may be useful in resolving unexpected problems with these analyzers. This discussion is not meant to be exhaustive or comprehensive in detail. More thorough discussions can be found in the analyzer operation manuals, and should be included in SOPs developed for these analyzers. Example SOP's prepared by EPA are included as Appendix B of the Technical Assistance Document (TAD) for Precursor Gas Measurements in the NCore Multi-pollutant Monitoring Network Version 4 (EPA-454/R-05-003).

Preventive Maintenance

Routine preventive maintenance procedures should be in place to prevent down-time and data loss. Management and field operators should jointly develop their preventive maintenance program. A program designed by persons unfamiliar with analyzer operations may include unnecessary items or omit mandatory ones. Several factors linked to shelter and sampling manifold design can contribute to data loss. SO_2 values can be low if the sample probe, manifold, and lines are dirty, cracked, or leaky. The sample probe and manifold should be cleaned at least every six months. Sampling lines should be replaced every two years. Teflon® filters used in the sampling train to remove fine particles may need to be replaced as often as every week, depending on the condition of the filter and the particulate loading around the monitoring site.

Table 5-1 illustrates items that monitoring agencies should include in their preventive maintenance program for high sensitivity SO_2 monitoring.

Item	**Schedule**
Replace particle filter	Weekly
Replace internal span permeation tube (if applicable)	Annually
Perform pneumatic system leak check	At least quarterly
Inspect internal, external tubing; replace if necessary	At least quarterly
Rebuild or replace pump	Annually
Replace UV lamp	As needed
Clean optic bench	As needed
Replace PMT	As needed

In addition to a schedule, the preventive maintenance plan should also include more detailed task descriptions, such as illustrated below:

- Because the analyzer pneumatic system requires so much preventive maintenance, the tubing, solenoids, and pump should be inspected regularly. Cracked tubing or loose fittings can cause the instrument to analyze room air rather than ambient air and lead to invalid data. A faulty pump can also cause problems with pneumatic systems. When oscillations in the flow rate force the operator to adjust the flow continually, the pump is failing and should be either repaired or replaced. The pump should be rebuilt or replaced when it is unable to maintain a vacuum of at least 25 inches of Hg.

- Check the instrument for vibration. When pumps get old, they sometimes will vibrate more than is normal. If this occurs, it can cause cracks if the tubing is touching another surface.

- Consult the analyzer operations manual for complete details on operation and maintenance.

Troubleshooting

High sensitivity SO_2 analyzers are subject to many factors that can cause inaccurate measurements or down-time. Table 5-2 summarizes common problems seen with high sensitivity SO_2 analyzers, their possible causes, and possible solutions. More specific information can be found in the manufacturer's operations manual.

Table 5-2. Instrument troubleshooting for precursor SO_2 analyzers.

Problem	Possible Cause	Possible Solution
Noisy output	Defective DC power supply	Replace power supply
	Dirty optics	Clean optics bench
	PMT failure	Replace PMT
High positive zero drift	Defective bandpass filter	Replace filter
	PMT failure	Replace PMT
No response to span gas	UV source is defective	Replace UV lamp
	UV power supply defective	Replace UV power supply
	PMT failure	Replace PMT
Zero output at ambient levels	Pump failure	Check pump
	UV lamp failure	Replace UV lamp
	UV power supply defective	Replace power supply
	PMT failure	Replace PMT
No flow through analyzer	Pump failure	Replace/ rebuild pump head

When troubleshooting, an operator must constantly be aware of environmental factors that may affect the instruments. Environmental factors can also cause sporadic problems that can be difficult to diagnose. Examples of factors that may affect the performance of the high sensitivity SO_2 analyzers are:

- Variable shelter temperature (fluctuations greater than several degrees);
- Excessive vibration from other equipment;
- Voltage instability (e.g., fluctuations in the 110 VAC line voltage);
- Air conditioning system blowing on the instrument; and,
- Frequent opening of the door of the shelter.

References

NOTE: REFERENCES WERE NOT PROVIDED BY THE AUTHORS OR WERE DELECTED FOR THIS CHAPTER (EPA 464, July 1983).

EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards, EPA-600/R-97/121. U.S. Environmental Protection Agency National Exposure Research Laboratory Human Exposure and Atmospheric Science Division Research Triangle Park, NC. September 1997.

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Instruction Manual, *Model 100A Sulfur Dioxide Analyzer,* Teledyne Advanced Pollution Instrumentation (T-API), San Diego, CA, February 2006.

Instruction Manual, *Model 43C Pulsed Fluorescence SO2 Analyzer*, Thermo Electron Corporation Environmental Instruments, Franklin, MA, April 2004.

Technical Assistance Document (TAD) For Precursor Gas Measurements in the NCore Multi-Pollutant Monitoring Network, Version 4, EPA-454/R-05-003, September 2005.

40 CFR 50

40 CFR 53

"National Ambient Air Monitoring Strategy," U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC 27711, Final Draft, April 2004.

Chapter 6

Ozone Measurement Principle and Calibration Procedure

Introduction

The ozone reference measurement principle and calibration procedure, promulgated in 1971 and amended in 1979, is based on detection of chemiluminescence resulting from the reaction of ozone with ethylene gas. Later, Rhodamine B, an organic dye embedded in a disc, was approved for use in place of ethylene to detect chemiluminescence. But neither method was problem-free. The flammability of ethylene was a constant concern, especially when monitoring was conducted in or near a public facility. The Rhodamine B analytical system did not regain a stable baseline rapidly enough after exposure to ozone. Thus, when UV analyzers were first approved as equivalent methods in 1977, they gained rapid, almost universal acceptance. Today, users have their choice of many approved UV instruments from several manufacturers. For more information on reference and equivalent methods, see Appendix 1(40 CFR Part 53).

Ozone in smog is formed by sunlight reacting with oxides of nitrogen (NO) and volatile organic compounds (VOCs) discharged into the air from gasoline vapors, solvents, fuel combustion products, and consumer products. Atmospheric conditions frequently transport precursor gases emitted in one area to another where the ozone-producing reactions actually occur. Since ozone is not emitted directly, but rather forms in the atmosphere from precursors gases, it is considered a "secondary pollutant." A discussion of precursor gases responsible for the formation of ozone is discussed in Chapter 7 of this manual.

The discussion in this chapter will focus on the application of the UV photometric method for the determination of ozone in ambient air.

Measurement Principle - Ultraviolet Absorption by Ozone

The analytical principle is based on absorption of UV light by the ozone molecule and subsequent use of photometry to measure reduction of the quanta of light reaching the detector at 254 nm. The degree of reduction depends on the path length of the UV sample cell, the ozone concentration introduced into the sample cell, and the wavelength of the UV light, as expressed by the Beer-Lambert law shown below:

(Eq. 6-1) $I = I_o \exp (-\}LC)$

where:

I = light intensity after absorption by ozone
I_o = light intensity at zero ozone concentration
$\}$= specific ozone molar absorption coefficient
L = path length
C = ozone concentration

The air sample is drawn into an optical absorption cell where it is irradiated by a low pressure, cold cathode mercury vapor lamp fitted with a Vycor sheath to filter out radiation with a wavelength of less than 254 nm. A photodetector, located at the opposite end of the sample cell, measures the reduction in UV intensity at 254 nm caused by the presence of ozone in the sample cell. To compensate for possible irregularities in output, another photodetector is used in some instruments to monitor the intensity of the mercury vapor lamp.

Although some ozone analyzers measure reference and sample air simultaneously using two absorption cells, most analyzers alternate these measurements, using only one cell. In the first part of the cycle, sample air is passed through a scrubber with manganese dioxide to remove ozone. The scrubbed sample air then enters the sample absorption cell to establish a reference light intensity at zero ozone concentration (I_o). In the second part of the cycle, sample air is re-directed to bypass the scrubber and enter the sample cell directly for measurement of the attenuated light intensity (I). The difference is related to the ozone concentration according to the Beer-Lambert law shown above. Thus, ozone in a sample stream can be measured continuously by alternately measuring the light level at the sample detector, first with ozone removed and then with ozone present.

Any ozone analyzer used for routine ambient air monitoring must be calibrated against a suitable ozone primary standard or a secondary standard directly traceable to a primary standard. An ozone primary standard is a photometer similar to a UV analyzer that meets the specifications in 40 CFR 50, Appendix D.

MONITORING/CALIBRATION APPARATUS AND MATERIALS

Because of the complexity of ozone monitoring equipment and procedures, this Section includes much more information than the customary list of equipment and supplies, to give field operators an in-depth understanding of their task and tools.

Monitoring Apparatus

UV Ozone Analyzer: Continuous air monitoring analyzers are commercially available from a number of vendors. The design of a UV ozone analyzer is similar to that of the photometer, but with one important difference. An ozone analyzer uses a special internal scrubber that removes ozone but not other gases to provide a zero-concentration ozone reference for the analyzer's zero reference. Maintaining the distinction between an analyzer and a photometer is very important. The term "analyzer" is reserved for the air monitoring instrument, the term "photometer" for the calibration standard instrument. For use in State and Local Air Monitoring Stations (SLAMS) networks, an analyzer must be one designated by EPA as an equivalent method under 40 CFR 53 (40 CFR 58, Appendix C, Section 2.1.)

Ozone analyzers have three major systems: the optical system (or "optic bench", as frequently used by the instrument manufacturers), the pneumatic system, and the electronic hardware. Each is described below.

(1) Optical System: Generally consists of the measurement cell or cells, a UV lamp, and a UV detector. The cells are usually made of aluminum, glass, or stainless steel tubes that can be sealed against leakage; the ends are either open or made of glass. The internal cell coating can vary, including Kynar, Teflon, glass, or stainless steel. The system should be easily accessible for preventive maintenance because particulate matter can collect in the cells and affect transmittance of light.

(2) Pneumatic System: Consists of sample probe, sample inlet line, particulate filter, solenoid valves, scrubber, internal tubing, flowmeter, and pump, all used to bring ambient air samples to the analyzer inlet.

(3) Electronic Hardware: The part of the analyzer that generally requires little or no maintenance. If the instrument is operated above the manufacturer's recommended temperature limit, however, individual integrated chips can fail and cause problems with data storage or retrieval.

Field operators should consult the manufacturer's operations manual for detailed, step-by-step instructions on how to use their particular analyzer. This Section discusses topics that are more generally applicable to analyzers as a whole.

A summary of one analytical cycle for a single-path instrument widely used in the determination of ozone in ambient air is described below. See also Figure 6-1.

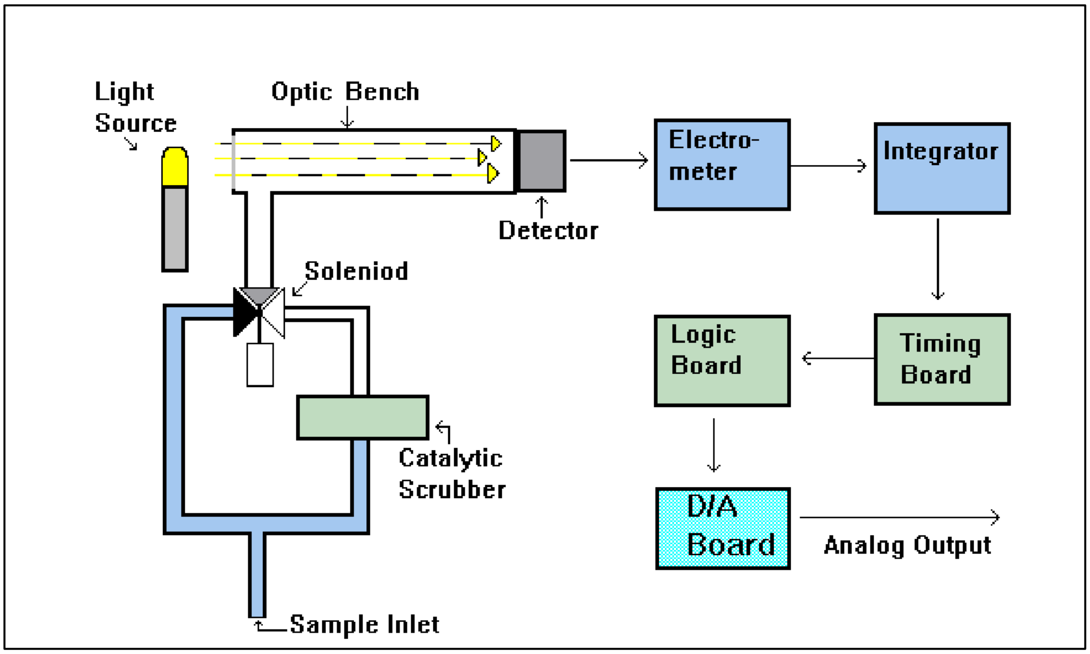

Figure 6-1. Ozone analyzer

The ozone analyzer is assumed to be attached to a data acquisition system (DAS). A timing circuit board regulates the analyzer cycle, which begins with the integrators cleared and deactivated. The memory circuit, digital display, and analog converter hold the values measured in the preceding cycle. The solenoid valve is then de-energized and sample air is drawn through the ozone scrubber into the absorption chamber. After the absorption chamber is purged with scrubbed air for a given time (usually 5-10 seconds), the integrators receive a signal to begin. They then measure the light transmittance received by the 254 nm wavelength-specific detector and transfer it to the logic board for storage.

After a pre-set time, often about 5 to 20 seconds but depending on the instrument, the solenoid is energized. The sample air is allowed to flood the optic chamber. If ozone is present in the sample air, the transmittance will be less. A ratio is then derived and the concentration calculated automatically. On-board electronics can measure environmental conditions inside an instrument and adjust the output accordingly. Some ozone analyzers, for instance, automatically correct the output for the internal temperature and barometric pressure of the optic cell.

Calibration Apparatus

The following equipment is required for calibration of an ozone analyzer.

Ozone Transfer Standard: A transfer standard, such as an ozone analyzer or ozone generator, that has been certified as a transfer standard against the local primary standard in accordance with stipulated procedures. A primary ozone standard may also be used directly for calibration, in which case it should be intercompared periodically with another primary ozone standard to check its veracity.

Ozone Generator: A generator providing stable ozone concentrations that can be varied manually or by automatic electronic feedback circuitry. If the transfer standard is an ozone generator, no other ozone generator is needed.

Zero Air Generator: Zero air is required for the calibration of ozone instruments. This air must be ozone-free to 0.001 ppm, and also free of nitric oxide (NO), nitrogen dioxide (NO_2), particulates, and hydrocarbons. Although there are many commercially available zero-air systems, zero air can also be generated by using a series of canisters that contain activated carbon, Purafil ™, and desiccant. Because NO may be difficult to remove, frequent changing of the carbon or use of an NO-to-NO_2 converter may be necessary. When such a converter is used, test the output with an NO/NO_x analyzer to ensure that the residence time in the system is long enough for complete conversion of NO to NO_2. The desiccant used with the zero-air system should be changed regularly. A canister system set up with a pump and surge tank can provide a cost-effective zero-air system. If a zero-air system is created, the moisture content must remain constant. Changing humidity can affect the response of UV photometers. Very dry zero air may also be a problem. The scrubber needs time to adjust if the zero air is much drier than the ambient air. Further discussion of preparation of zero air can be found in Chapter 4, *Generation of Test Atmospheres*, of this Manual.

***Output Manifold*:** Although the output manifold can be constructed of borosilicate glass, Teflon, or stainless steel, glass is recommended. The manifold must have an opening that vents excess air to the atmosphere such that the pressure in the manifold is as close to atmospheric pressure as possible. If ozonated air is delivered under too high a pressure, the ozone readings obtained will not be representative. Manifolds collect particulate matter on the internal walls because neither zero air nor sample air is totally particulate-free. Because stainless steel or Teflon manifolds are opaque, it can be difficult to determine whether they are collecting particulates. A transparent glass manifold can be inspected easily and cleaned readily by rinsing with distilled water and air drying.

***Barometer*:** The internal barometric pressure of a transfer standard needs to be determined accurately if measurements are made above 1000 feet in elevation (approximately 730 mm Hg). Many commercially available analyzers or photometers with built-in barometric pressure sensors automatically correct the measured ozone values to 760 mm Hg. If automatically adjusting instruments are not available, pressure corrections need to be made manually.

***Temperature Sensor*:** The internal temperature of a photometer must be measured accurately. Many newer photometers have built-in temperature sensors to automatically correct the measured ozone values to 298^0K. If automatic adjusting instruments are not available, temperature corrections need to be made manually.

Materials

***Tubing and Fittings*:** Teflon and Kynar are two inert materials that should be used exclusively throughout the system. Stainless steel tubing should be avoided because it is expensive, hard to clean, and can develop micro-cracks that are difficult to detect. Teflon tubing is the best choice because it can be examined and discarded if particulate matter is collecting in it. It is also very pliable. All fittings and ferrules must also be made of Teflon or Kynar.

ANALYZER CALIBRATION

Table 6-1 summarizes the many calibrations requirements for the UV analysis of ozone. The text of this Section then describes these requirements in detail.

Calibration Standards

No Standard Reference Materials (SRMs) exist for ozone because ozone is unstable in cylinders. Therefore, ozone standard concentrations must be generated dynamically *in situ*, either with (1) an ozone generator certified as an ozone transfer standard; or (2) an uncertified ozone generator whose output concentration levels are assayed with a primary standard photometer or an ozone assay instrument certified as an ozone transfer standard.

Ozone can be generated by irradiating zero air with UV light from a cold cathode mercury vapor lamp. To be useful for calibration, the generated ozone concentrations must be stable and reproducible over a 15- to 30-minute time period. The ozone concentration can be modulated in several ways: (1) increasing or decreasing the intensity of the lamp to raise or lower the ozone concentration while keeping the air flow constant; (2) increasing or decreasing the air flow while keeping the lamp intensity constant; and (3) mechanically altering the intensity of the radiation using a variable shutter or sleeve. Most commercially available calibration systems with internal ozone generators modulate the ozone concentration by changing the intensity of the generating lamp electronically.

Table 6-1. Calibration Requirements for Ozone

Requirement	Frequency	Acceptance Criteria	Reference	Information/Action
Calibration Photometer linearity test	?	Linearity error <5%	40CFR 50 App. D, S.5.2.3 1/ EPA-600/4-79-056	Check/verify accuracy of flow dilution. Redo analysis. If failure persists corrective action required. See 2nd reference.
Transfer standard Qualification - Precision	1/3 mo.	4% ±4ppb (whichever greater) RSD of slope ≤3.7%	EPA-600/4-79-056 S.4 EPA-600/4-79-056 S.6.5	6 comparison runs that include, at minimum, 6 concentrations including 0 and 90 + 5% of upper range.
Certification to reference standard	1/year	Quantity of intercept ≤1.5% new slope = ±0.05 of previous	EPA-600/4-79-056 S.4 EPA-600/4-79-056 S.6.5	6 comparison runs that include, at minimum, 6 concentrations including 0 and 90 + 5% of upper range.
Reference Photometer Certification		Slope =1± 0.01, intercept < 3ppb	See Note 2/	9 replicate analysis over 12 conc. ranges. Disagreement must be resolved. EPA SRP rechecked with NIST. If OK, network SRP must be repaired.
Zero/Span Check – Level I	1/ 2 weeks	Zero ± 20 ppb Span ± 20 % Zero ± 10 ppb Span ± 15%	Vol II-S.12.6 “ Vol II-S.12.6 “	If calibration updated at each zero/span- Invalidate data to last acceptable check, adjust analyzer, perform multi-point calibration. If fixed calibration used to calculate data. Invalidate data to last acceptable check, adjust analyzer, and perform multi-point calibration.
Multipoint	upon receipt upon zero/span adjustment. 1/ 6 mo.		40CFR 50 App. D, S.5.2.3 EPA-600/4-79-057 S.5 Vol II-S.12.2	5 or more upscale calibration points.
Performance Evaluation NPAP State Audits	1/year-selected 1/yr sites	Mean absolute % diff. ≤ 15% State requirements	Vol II-S.16.3 No ref.	Use information to inform reporting agency for corrective action and technical systems audits.

1/ - reference refers to the QA Handbook for Air Pollution Measurement Systems, Volume II. The use of “S” refers to sections within Part I of the Handbook. The use of “MS” refers to sections of the method for the particular pollutant.

2/ - Protocol for the recertification of standard reference photometers in the EPA standard reference photometer network. 1996. TRC Environmental Corporation. Chapel Hill, NC 27514.

Primary Standards

EPA has established UV photometry as the primary standard for ozone concentrations (40 CFR 50, Appendix D). Ozone primary standard concentrations are determined by a primary standard photometer. Ozone photometry is based on the Beer-Lambert law as previously discussed. A primary standard ozone photometer is an instrument that measures ozone using the Beer-

Lambert law at 254 nm, uses the absorption coefficient for ozone (308.8 $\text{atm}^{-1}\text{cm}^{-1}$ at 273^0K and 760 mm Hg), and meets all other requirements. Most commercially available photometers make these corrections automatically. An auxiliary ozone generator is also required to provide stable ozone concentrations to be assayed by the photometer.

An ozone standard photometer is very similar to the ozone analyzer earlier, but has no built-in scrubber for removing ozone. Therefore the photometer must be supplied with zero air from the same source that supplies zero air to the ozone generator.

Standard Reference Photometers

EPA and the National Institute of Standards and Technology (NIST) jointly developed a special, highly accurate standard photometer known as a Standard Reference Photometer (SRP) to serve in lieu of an SRM for ozone concentrations. NIST maintains one or more "master" SRPs. EPA maintains 10 other SRPs: one in Research Triangle Park, NC; seven in EPA Regional Office laboratories; one at the California Air Resources Board; and a traveling one used for intercomparisons. Other SRPs are located in foreign countries.

Each SRP is a standard in its own right and is not "calibrated" against the NIST unit. Instead, all SRPs are intercompared periodically to verify that they all agree with one another and to establish NIST-traceability. If one does not agree with the others, it is not recalibrated--it is repaired. The EPA SRPs provide NIST traceable ozone standards that are accessible to states and local agencies for verifying their own local primary standards. In some cases, the SRPs may also be available for certification of transfer standards.

Local Primary Standard

Each monitoring agency needs its own local primary standard photometer that serves as the single master standard for all ozone calibrations carried out by the agency. This local primary standard photometer is operated as described in Technical Assistance Document (TAD) for Calibration of Ambient Ozone Monitors, EPA-600/4-79-057(1979). Other ozone photometers or transfer standards are used as working standards to calibrate the ozone monitoring analyzers. These transfer standards are all referenced to the local primary standard. Calibration photometers are commercially available from a number of vendors, or a UV analyzer can be modified to become a calibration photometer.

Verification of Local Primary Standard

Because even primary standard photometers can malfunction, each local primary standard should be compared at least annually to an SRP to reverify its accuracy and recertify its NIST traceability. Although a local primary standard may be moved to an SRP laboratory for the comparison, a transfer standard that has recently been recertified against the local standard is usually moved instead, to protect the local standard from damage during transit.

The local primary standard photometer is not calibrated against a verified SRP, because it is a standard in its own right. Instead, it is compared with the SRP to verify its continued accuracy. If there is a substantial difference (more than ± 5%, preferably ± 3%) between the local standard and the SRP, the local standard is considered to be malfunctioning and must be repaired and re-verified before further use.

In a typical verification of a local primary standard, a six-point calibration (a 1x6) of a transfer standard against the local primary standard is performed throughout the operating range, generally 0-1.000 or 0-0.500 ppm, and including zero, to establish a linear relationship between the transfer standard and the local primary standard. If the transfer standard is an established one with a recent 6x6 calibration (a 1x6 done on six days within a 14-day period using the same ozone concentrations), use that calibration data instead. Then perform a similar comparison of the transfer standard against the SRP.

The two linear regressions (between transfer standard and SRP and between transfer standard and local primary standard) are then compared. If the linear regressions against the transfer standard are within 1.00 +/- 0.03 on slope and 0.003 ppm on intercept, then the local primary standard is operating within acceptable limits.

Agencies needing SRP verification should contact their EPA Regional office. The Regional SRP laboratory will contact them and provide guidance for conducting the intercomparison.

Transfer Standards

A transfer standard is a secondary standard that is used to transfer the accuracy (or authority) of the local primary ozone standard to the ozone analyzers at the monitoring sites. A transfer standard is first calibrated against the local primary standard and then used in the field to calibrate ozone analyzers. A transfer standard may be an ozone generator or an ozone photometer. For the latter, a stable auxiliary ozone generator is also required to produce certifiable ozone concentrations. All transfer standards must meet the qualification requirements described in the TAD - Transfer standards for calibration of air monitoring analyzers for ozone, EPA-600/4-79-056. Commercially available transfer standards usually have a built-in ozone generator.

Clean Teflon tubing should be used between the primary and the transfer standards. The zero air should have less than 0.001 ppm of ozone. If the transfer standard has a zero air scrubber, the transfer standard should be plumbed to take in zero air through that scrubber during the zero air cycle. Normal manufacturer's recommended maintenance procedures should be performed for the primary standards and for cleaning the optical system. To eliminate the need for frequent cleaning of the optical system, a Teflon filter (pore size of 10 microns) should be used on the inlet of the primary standard.

Temperature- and pressure-sensing hardware must be calibrated annually. The temperature-sensing unit should be submersible and compared against a NIST-traceable thermometer in water at three different temperatures. The barometer should be compared against a Fortin barometer or equivalent.

Calibration/Certification of Transfer Standards

Several conditions must be met before an instrument can be certified as a transfer standard.

- The transfer standard must be capable of generating or assaying ozone concentrations very precisely and repeatably. The same instrument must never be used both as a transfer standard and as an analyzer to collect data. If so, the authority of the transfer standard is voided and can be reestablished only by a new comparison.

- A transfer standard has no intrinsic authority of its own and must be referenced and certified to a primary standard before use for calibrating analyzers.

- Once authority has been established, a transfer standard should be recalibrated or recertified at least every three months against a primary standard.

- Photometers, UV analyzers, and ozone-generating units are the preferred transfer standards.

- Transfer standards are always used with clean, filtered zero air.

- A transfer standard can be operated with or without a ozone-zero air scrubber. If a scrubber is used, it should be changed regularly, depending on how much the photometer is used between recertifications and on the manufacturer's recommendation. Scrubbers should be replaced at least annually. If an internal scrubber is not used, then some type of external scrubber, such as activated charcoal in an air-tight canister, is needed during the zero-air cycle. Once certified against a local primary standard, a transfer standard must keep the same scrubber configuration during use.

- A transfer standard must be a rugged device readily transportable, yet light enough to be carried across difficult terrain. It should be shipped in foam-lined, impact-resistant plastic containers, and secured by vehicle seat belts whenever possible.

- Documentation of calibration and certification to the local primary standard must always remain with the transfer standard for ready access if data collection procedures are questioned during audits. An accompanying folder or logbook should summarize the tests that have been performed on the instrument to establish authority to a primary standard.

- The primary and transfer standards must analyze the same air under the same atmospheric conditions. The manifold to which they are connected must have an opening large enough so that excess air can leave the manifold without any back pressure. Many commercially available photometers have built-in ozone generators and calibration manifolds. If the transfer standard has an ozone generator or manifold, use as short a length of tubing as possible from the manifold to reduce line loss to the standard.

- If an independent ozone generator is used, then the lines to the primary and transfer standards should be approximately the same length. Use only Teflon lines.

- Use the same zero air for the primary and transfer standards if the zero air scrubber is removed from the transfer standard.

- Vent the ozone to the outside, if possible. Ozone exposure in an enclosed area can contribute to health problems.

- Assign one person (and a back-up) to performing the intercomparisons to reduce problems attributable to operator variability.

Perform a 1x6 comparison by attaching Teflon lines from the inlet of the transfer standard to one manifold port and from the inlet of the primary standard to another port. Thereby, both instruments can sample the atmosphere in the manifold simultaneously. See Figures 6-2, 6-3, and 6-4.

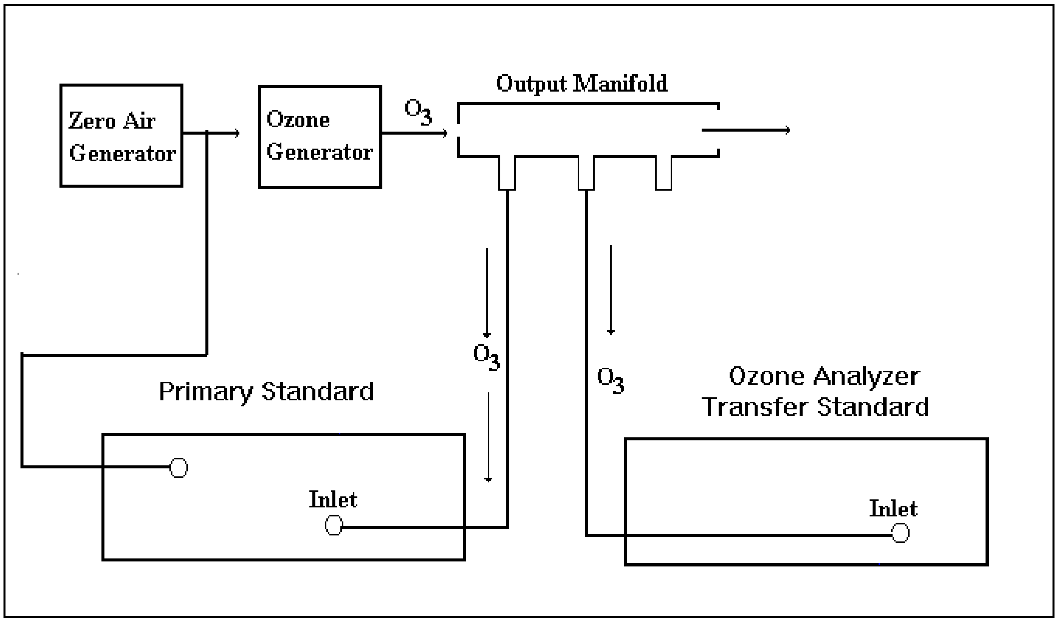

Figure 6-2. Calibration of an ozone analyzer-type transfer standard

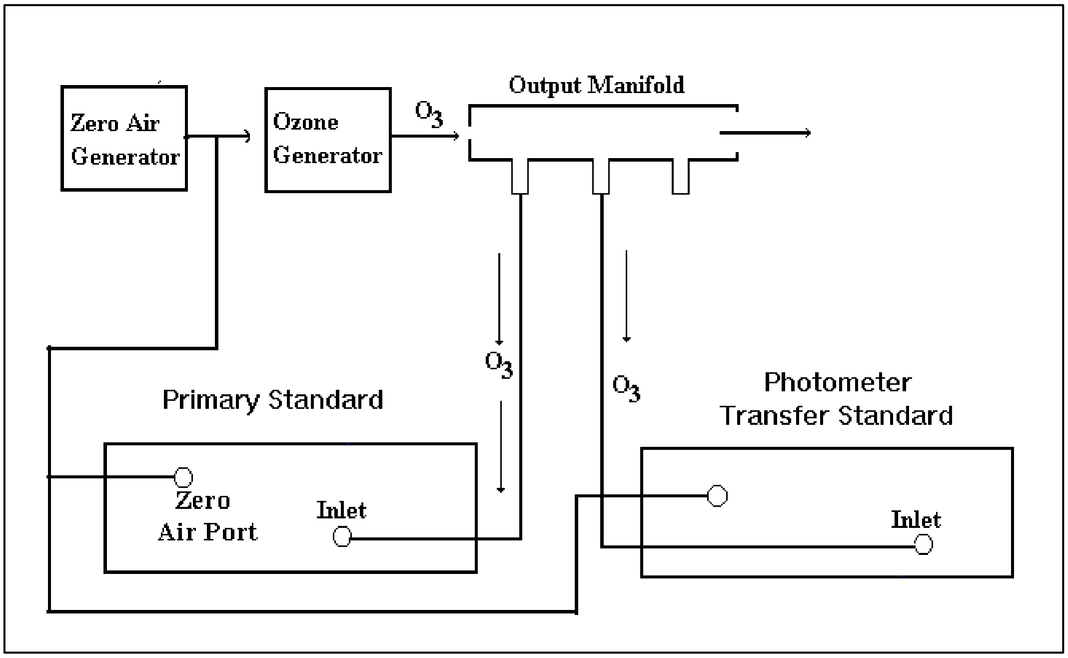

Figure 6-3. Calibration of a photometer-type transfer standard

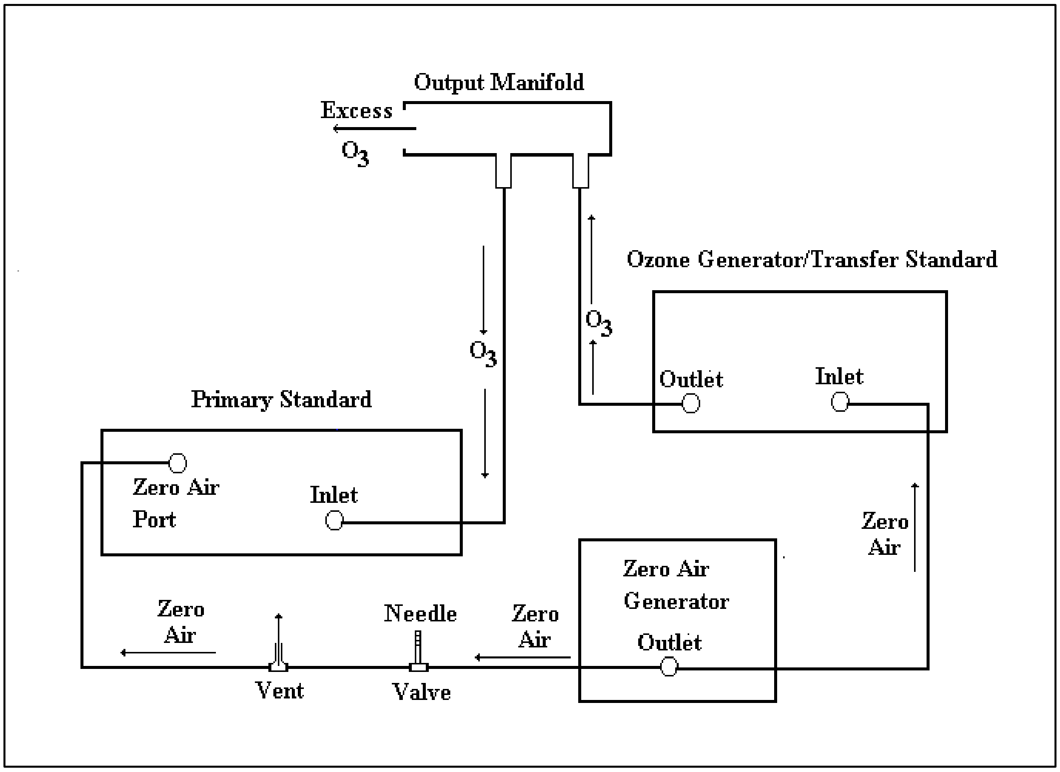

Figure 6-4. Calibration of an ozone generator-type transfer standard

Procedure for the Calibration of a Transfer Standard

1. Allow the transfer and primary standards to warm up properly. Generally, one hour is sufficient. Consult the manufacturer's operating manual for details.

2. Record the span and the count frequency settings, temperature, and barometric pressure (if applicable) on both the primary and transfer standards.

3. Attach the inlet of the primary and transfer standard to the ozone manifold. Make sure that there is proper venting of ozonated air.

4. With the ozone lamp off, allow both the primary and the transfer standards to stabilize to zero air. Record 10 readings from the primary and the transfer standard simultaneously. (If an ozone generator is used as a transfer standard, a control setting rather than a reading may need to be recorded.)

5. After 10 readings have been recorded, switch on the ozone lamp and set the lamp for 80-90% of the full scale of the ozone transfer standard.

6. Allow the primary and the transfer standard to stabilize at this ozone concentration and record 10 readings from the both instruments simultaneously.

7. Repeat the two previous steps at each of at least four lower ozone concentrations.

8. After six concentrations of ozone have been tested against the primary and transfer standard and all values have been recorded, turn off the ozone lamp and allow both instruments to sample zero air.

9. Record the temperature and barometric pressure of the primary standard once the tests are finished. Then examine the data for evidence of temperature or pressure instability.

10. Average all data points at each level. Perform a linear regression on this data set, following instructions given in the TAD - Transfer standards for calibration of air monitoring analyzers for ozone, EPA-600/4-79-056.

11. Repeat this entire procedure on five more days within a two-week period to complete the 6x6 comparison.

Ozone Analyzer Calibration

Once a primary standard and all transfer standards have been selected and authority established, the ozone analyzer can be calibrated by referencing its ozone response at the monitoring station against the transfer standard.

Many agencies use an on-site mass-flow controlled calibration unit with an ozone generator to generate ozone standard concentrations. If no such ozone source is available, then use either the ozone generator of the transfer standard or the one built into the photometer.

A multipoint calibration should be performed at least every six months.

Multipoint Analyzer Calibrations

1. A multipoint calibration includes a minimum of four points (three spaced over the expected range and a zero point), each collected simultaneously from the transfer standard and the ozone analyzer. The following steps outline the multipoint calibration procedure.

2. Allow both the transfer standard and the ozone analyzer to warm up properly. Usually, one hour is sufficient, but consult the manufacturer's instruction manual for specific details.

3. Record the span and frequency setting and the temperature and barometric pressure (if available) for the ozone analyzer and transfer standard, to use as QC checks.

4. If using an on-site ozone generator, flood the manifold and attached ozone analyzer with ozone. Then attach the transfer standard to the manifold. Take readings and compare. If the photometer has a built-in ozone generator, then attach the inlet of both the photometer and the analyzer to the internal manifold of the photometer. Make sure there is proper venting of any excess ozonated air.

5. If the station is equipped with an on-site calibration unit, start production of zero air, mark the strip chart, and flag the DAS data. With the ozone lamp off, allow both ozone analyzer and transfer standard to stabilize to zero air. When stability is satisfactory, record 10 readings from the DAS ozone channel and transfer standard simultaneously.

6. Switch on the ozone lamp and set it to 80-90% of full scale of the transfer standard. Allow the analyzer and transfer standard to stabilize at this reading.

7. Then record 10 readings from the DAS ozone channel and the transfer standard simultaneously.

8. Lower the ozone lamp setting to 40-50% of full scale. Repeat the previous two steps.

9. Lower the ozone lamp setting to 15-20% of full scale. Repeat as above.

10. Once three ozone levels are tested and all values recorded, turn off the ozone lamp and allow both instruments to sample zero air to see if the baseline of the transfer standard has drifted.

Once the tests are completed, record the temperature and barometric pressure (if available). Perform a linear regression and report both the raw data and the regression results to the data handling group. Acceptance criteria for the linear regressions are left to the discretion of the monitoring agency, but the following are suggested: slope, 1 ± 0.10; intercept, ± 0.010; correlation coefficient, > 0.995. Whatever criteria are selected, the instrument still must pass audit tests, which require a difference of no more than ± 15%. These regular multipoint calibrations must be done at least every six months. In between times, however, other calibrations and checks are used whenever analyzer zero or span drift has been detected.

Level I Calibrations

Level I calibrations consist of a zero-air point and an upper-level point, usually between 75% and 90% of full scale. With the integration of DAS hardware and software, they can be performed automatically. A DAS calibration system is especially recommended for greater precision and accuracy at remote locations. Many of these systems are available commercially. See Figure 6-5.

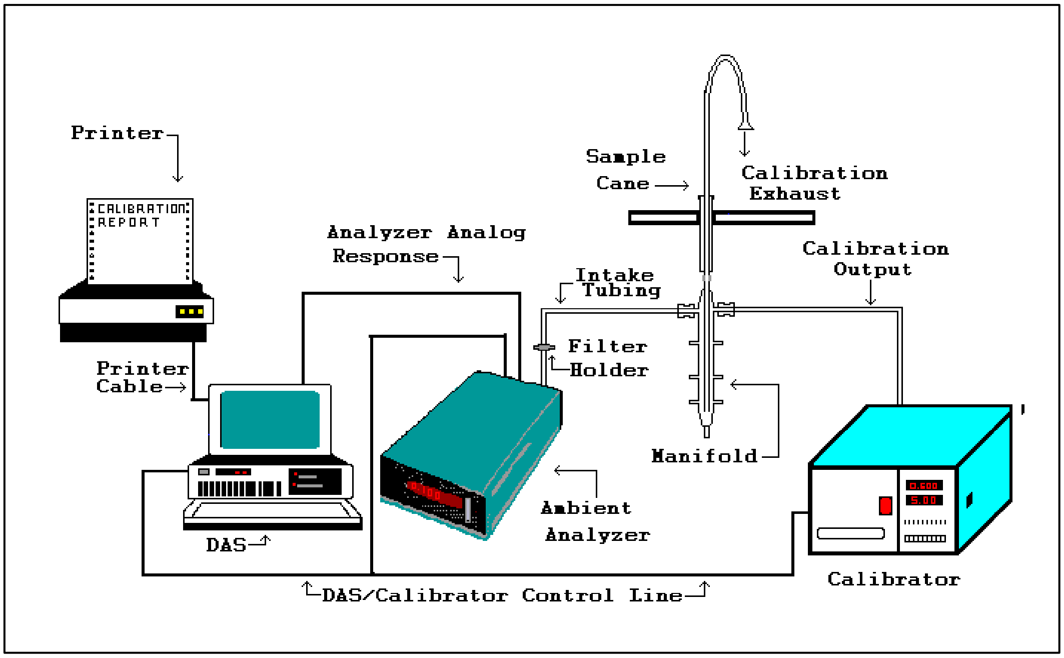

Figure 6-5. DAS calibration system

Calibration/Certification of On-Site Transfer Standard

If an ozone generator is used as the ozone source, there must be some method to transfer authority from a mobile transfer standard to an on-site transfer standard. This can be done by generating ozone with the onsite generator and allowing the transfer standard to sample the ozone concentrations at different levels. If this calibration is performed quarterly, the authority from the mobile transfer standard can be transferred to the on-site generator. Then the DAS-generator combination can be set up to perform automated Level I calibrations as specified by the operating agency. If an operator performs Level I calibrations manually, the transfer standard can be substituted for the calibrator.

Level II Zero/Span Checks

Level II zero/span checks are quick tests used to detect analyzer drift. They cannot be used for data validation, however, because they use an uncertified ozone standard not traceable to a primary standard.

INTERFERENCES

Preventing interferences is crucial to the accurate measurement of ozone. This section describes the three most common interferences--water vapor, aromatic hydrocarbons, and mercury--and recommends procedures to minimize these interferences.

Overview

UV ozone analyzers measure ozone concentration by absorption of electromagnetic radiation at a wavelength of 254 nm. Any other gas in the air sample that also absorbs at that wavelength could present an interference. The UV analyzer operates by comparing absorption measurements of the sample air with measurements of the same sample air after removal of only the ozone by an ozone scrubber.

Ideally, a gas that absorbs at 254 nm will do so equally in both measurements, and the effect will cancel. The scrubber must remove 100% of the ozone while quantitatively passing other gases that absorb at 254 nm. Some gases, however, may be partially or temporarily absorbed or adsorbed by the scrubber, such that their concentration is not equal in both measurements. An interference can occur when a gas absorbs at 254 nm or produces some other physical effect (such as water condensing on scratches in the cell window), and does not pass freely through the ozone scrubber. Hence, proper scrubber performance is critical to minimizing interferences.

Negative interferences result from incomplete removal of ozone by the scrubber and from loss of ozone by reaction or adsorption in dirty inlet lines, filters, analyzer plumbing components, and the measurement cells, particularly with long residence times. Condition all sample lines and filters by exposing them to high concentrations of ozone (>400 ppm) for at least 30 minutes. New tubing and filters that are not conditioned will take up ozone for some time.

Ozone breakthrough has been shown to be a transient problem occurring primarily under humid conditions. Before use in high humidity environments, new scrubbers may need to be pre-treated by proprietary methods recommended by the manufacturer to saturate ozone adsorption or reaction sites. Ozone breakthrough can also occur in dry conditions if the scrubber is not replaced according to the manufacturer's recommended schedule.

Three common positive interferences for UV ozone analyzers are discussed below. (Note: The guidance provided for common interferences is the current best judgment based on available information and is subject to modification pending availability of further data. For further discussion see the document, *Determination of Ozone by Ultraviolet Analysis, A New Method for Volume II, Ambient Air Specific Methods, Quality Assurance Handbook for Air Pollution Measurement Systems, Final Draft, May 1, 1997.*

Water Vapor

A recent study showed conclusively that UV analyzers have negligible interference from water vapor in systems containing only ozone, water vapor, and zero air. The measured ozone concentrations were within 0.5 percent of the true ozone values at various test humidities. Even condensed water in the sampling line did not cause high ozone readings. This lack of water vapor interference is expected because water vapor absorption in the UV region is negligible above 186 nm. In contrast, chemiluminescence ozone analyzers have a well-documented water interference of about 3 percent per percent water in the air, over a range of 1 to 3 percent water, corresponding to dew point temperatures from about 9 to 24^0C.

Water vapor, however, can nevertheless affect UV-based ozone measurements under some conditions. When the humidity of the sample air is high enough to approach saturation, condensation of water may occur at various points in the sampling system or analyzer. Further, water vapor may be absorbed by the scrubber such that some period of time is required before the air leaving the scrubber is at the same humidity as the sample air. At high humidity, condensation can also occur on scratches in the cell windows. During transition periods when the humidity of the sample air is increasing, such condensation may even occur during the sample air measurement, but not during the zero ozone measurement, resulting in a positive interference.

High humidity or condensation in the sample air may also affect the ability of the scrubber to pass other potentially interfering gases, such as aromatic hydrocarbons. Although condensed water did not affect ozone measurements in clean air tests, condensation in a dirty inlet line and other inlet components -- especially particulate filters -- is notorious for reducing measured ozone concentrations.

Data quality will be enhanced by following the recommendations below.

- The best way to avoid condensation in the inlet sample air is to assure that the temperatures of all locations in the analyzer and sample inlet line remain above the dew point temperature of ambient air.

- Maintain the monitoring shelter at temperatures no lower than 26-27^{0}C (79-81^{0}F), if possible, in areas where dew point temperatures are high. Outdoor ambient air dew point temperatures can exceed 27^{0}C (80^{0}F) on hot, summer days, particularly in coastal areas or following rain. If the shelter temperature cannot be increased, wrap the inlet line and sampling manifold with thermal insulation.

- Make sure that air conditioners or cool air ducts do not blow directly on the analyzer or on the inlet line. Use a thermograph to monitor the shelter temperature near the analyzer for several days under a variety of weather conditions to ensure that the temperature does not get too low or too high when the air conditioner cycles on and off.

- Record the ozone analyzer output using a strip chart recorder, data logger with graphics capability, or similar method to plot 1-minute digital data for several days during humid weather. Look for abnormal characteristics such as cyclic patterns, long periods with little or no change in concentration, or unusually low readings when higher readings would be expected. Cyclic patterns, for instance, are frequently synchronized with the on-off cycles of the shelter air conditioner. All abnormal patterns should be investigated to see if they also represent errors in the ozone measurements.

Aromatic Hydrocarbons

Many aromatic hydrocarbons are known both to absorb light at 254 nm and to be "sticky"-- readily absorbed or adsorbed on surfaces exposed to air samples. Smog chamber studies producing ozone by irradiation of toluene/NO mixtures showed that benzaldehyde and other aromatic photo-oxidation products such as *o*-cresol and *o*-nitrotoluene were almost completely removed by ozone scrubbers used in ozone UV analyzers. Although scrubber retention of aromatic hydrocarbons produces a positive interference initially, the retained compounds may be released later when conditions change, giving rise to a negative interference. Under humid conditions, compounds may be desorbed from the scrubber.

Generally, aromatic hydrocarbons cannot be significantly removed from air samples without also altering the ozone concentration. Therefore the only practical way to avoid interference from these compounds is to avoid siting a UV analyzer in an area that may have significant concentrations of aromatic hydrocarbons.

Problems with hydrocarbon interferences can be minimized by taking the following precautions.

- Avoid sites near or downwind from asphalt plants, asphalt paving operations, chemical plants, and similar sources.

- Avoid large asphalt areas such as roadways and parking lots that can outgas significant aromatic hydrocarbon concentrations on hot, sunny days.

- Avoid local influence from hydrocarbons near motor pools, diesel fueling tanks, gas stations, thruways, tunnels, airports, and other areas of heavy motor vehicle traffic.

- Avoid highly urban or heavily polluted areas, if possible, to prevent interference from toluene, an aromatic hydrocarbon normally found in high concentrations in urban atmospheres.

- Avoid applying herbicide and pesticide formulations near the monitoring shelter, to prevent interferences from out-gassing of hydrocarbons used in the formulations.

- Use a non-UV type analyzer when an ozone monitoring site must be located in an area where aromatic hydrocarbon concentrations are high. Chemiluminescence ozone analyzers are not affected by interference from aromatic hydrocarbons and are recommended for such sites, but they are difficult to obtain because few manufacturers still make them. Another alternative is to use an open-path differential optical absorption spectrometer (DOAS) analyzer, which also is not affected by interference from aromatic hydrocarbons.

Mercury

Interference from mercury is generally not a problem at most sites because atmospheric concentrations are usually very low, but the possibility of locally high mercury concentrations in the vicinity of a monitoring site does exist. Local atmospheric contamination from mercury has been attributed to a wide variety of sources, ranging from dental fillings to herbicides used near a monitoring shelter.

Minimize the effect of mercury interference by taking the following precautions.

- Keep the monitoring station free of spilled mercury for measurement as well as health reasons.

- Inspect the area around a monitoring site for possible contamination from spilled mercury, application or disposal of mercury-containing chemicals, or other sources of possible mercury contamination.

- Never use a vacuum cleaner to pick up spilled mercury. More contamination can result if mercury vapor is spread throughout the area and liquid mercury remains in the bag. Instead, use a commercially available mercury clean-up kit that employs sponges and a bulb-type suction device.

- Examine ozone measurement data for unusual patterns or verify data with a non-UV ozone analyzer because the evidence of mercury contamination in the area may not be obvious.

Routine Checks and Preventive Maintenance

To determine whether the analyzer is working properly, field operators perform many routine operations every time they visit the monitoring station. Each agency needs to develop maintenance checklists or electronic spreadsheets to document that all required checks have been made. The lists and sheets should be useful both for collecting data and for assessing the quality of that data. Management must review them regularly and change them if necessary.

Preventive maintenance should prevent down-time and data loss. Management and field operators should jointly develop their preventive maintenance program.

Table 6-2 illustrates items that monitoring agencies should include in their ozone preventive maintenance program.

Table 6-2. Example of a Preventive Maintenance Schedule for Ozone Monitoring

Item	Schedule
Replace particle filter	Weekly
Perform Level I calibration*	Weekly
Perform electronic parameter checks	Weekly
Clean fan/fan filter	Semi-annually
Clean optic bench	Semi-annually
Perform multipoint calibration	Semi-annually
Replace zero air scrubber	Semi-annually
Inspect internal, external tubing; replace if necessary	Semi-annually
Replace UV lamp	As needed
Replace solenoid	As needed
Rebuild or replace pump	Every two years

* Weekly Level I calibrations should be performed only if nightly automated Level I calibrations are not performed.

In addition to a schedule, the preventive maintenance plan should also include more detailed task descriptions, such as illustrated below:

- Clean the optical cells with optical cleaning paper and Teflon tubing to prevent scratching. The cells must be re-installed without leaks.

- Because the analyzer pneumatic system requires so much preventive maintenance, the tubing, solenoids, and pump should be inspected regularly. Cracked tubing, loose fittings, and faulty solenoids can cause the instrument to analyze room air rather than sample air and lead to invalid data. Particles in the solenoid valve can cause an erroneous analyzer response because the valve may not close completely. A faulty pump or rotameter can also cause problems with pneumatic systems. When oscillations in the rotameter force the operator to adjust the rotameter continually, the pump is failing and should be either repaired or replaced.

- Always operate ozone analyzers with zero-air scrubbers. Change the scrubbers regularly, depending on usage, but at least every six months and before calibrations.

Consult the analyzer operations manual for complete details on operation and maintenance.

TROUBLESHOOTING

Ozone analyzers are subject to many factors that can cause inaccurate measurements or down-time. Consult the manufacturer's operations manual for detailed descriptions of troubleshooting procedures. The following text and table provide guidance on some of the more common problems likely to be encountered.

Environmental Factors

When troubleshooting, an operator must constantly think about environmental factors that may affect the instruments.

- Is the shelter temperature fluctuating too much (more than, say, 2-3^0C)?

- Is vibration from other equipment causing problems?

- Is voltage to the instrument stable? Power fluctuations in the 110V line can cause erratic performance.

- Is the air conditioning system blowing on the instrument, especially at a particular time each day?

- Does opening the door of the shelter cause variations of the data collected?

Environmental factors can also cause sporadic problems that can be difficult to diagnose. For instance, sunlight shining on an instrument may heat it, causing a temperature change and invalid readings. But as the sunlight moves away from the instrument, the problem disappears.

General Factors

Other factors linked to shelter and sampling manifold design can contribute to data loss. Ozone values can be low if the sample probe, manifold, and lines are dirty, cracked, or leaky. The sample probe and manifold should be cleaned every six months. Teflon lines should be replaced every two years. The10-micron filters used in the sampling train to remove fine particles may need to be replaced as often as every two weeks, depending on the condition of the filter and the particulate loadings around the monitoring site.

Instrument Troubleshooting

Table 6-3 summarizes common problems seen with ozone analyzers and photometers, possible causes, and possible solutions. More specific information can be found in the manufacturer's operations manuals.

Table 6-3. Instrument Troubleshooting for Ozone

Problem	Possible Cause	Possible Solution
Negative values	Weak UV lamp	Replace lamp
	Bad solenoid valve	Replace valve
	Low reading	Replace worn zero air scrubber
	Drifting photometer	Check electrometer voltage
	Flow rate too high	Decrease flow rate
	Flow rate too low	Increase flow rate
No display	No voltage to motherboard	Check power supply
	Bad power supply board	Replace power supply board
Excessive noise	Dirty optics	Clean optic bench
	Erratic block heater	Replace block heater
	Erratic lamp voltage	Check lamp driver board
	Leak in pneumatics	Perform leak test
Pump not working	A short in pump windings	Replace pump
	Pump bearings frozen	Replace pump bearings
	Pump diaphragm worn	Rebuild pump head
	Leak in pneumatics	Perform leak test
Photometer lamp will not light	Bad lamp driver	Replace lamp driver board
	Bad lamp	Replace lamp
No ozone readings	Saturated detector	Adjust detector
	Defective timing board	Replace board
	UV lamp not lit	Check electronics; replace lamp
Zero, then random, readings	Leak in pneumatics	Fix leak
	Defective timing board	Replace board

DATA ACQUISITION, CALCULATIONS, AND DATA REDUCTION

In the past, the most effective way to collect ozone data was on strip chart recorders. Today, due to advances in data storage and retrieval systems, most strip chart recorders are used as back-up systems. Some present day electronic data acquisition systems (DASs) are less expensive than a high quality strip chart recorder. Any DAS should still be used with a backup system as protection against data loss due to system failure.

Data Acquisition

Electronic data acquisition systems are widely used, and as shown below, have many advantages over strip chart recorders.

- **Accuracy.** A properly operating DAS usually collects data at rates of several times per second. The one-second values are calculated and stored until the end of the hour when the hourly ozone value is computed automatically. These hourly averages are more accurate than those from a strip chart because no human interpretation is involved.

- **Data collection options.** Instantaneous, short-term, and hourly data are collected and stored.

- **Data flags.** Data review parameters, such as maximum and minimum values, can be written into the software code to screen and flag suspect data.

- **Long-term storage.** Data can be stored indefinitely to provide a long-term storage device for many years of data.

- **Spreadsheet capability.** Newer systems allow calling up several parameters at one time to compare factors such as meteorological conditions by using a spreadsheet type of presentation.

- **Calibration control.** A DAS can control calibration equipment and record calibration data as they are being collected, making an excellent tool for use in remote locations.

Calculations and Data Reduction

The latest generation of data acquisition systems can be accessed remotely via modem and software so that a remote user can monitor pollutant levels and see the results of automatic calculations on a real-time basis.

Calibration checks are used as an indirect verification of DAS software and hardware. If a check is satisfactory, the entire data collection system, including the DAS, is assumed to be operating properly. If not, a search for the cause of the problem begins. Occasionally, a DAS chip fails and the board holding it has to be replaced.

Ozone data, like that for other gaseous criteria pollutants, are stored as hourly averages. Even though the 8-hour ozone standard replaced the 1-hour standard, States and local agencies continue to report hourly averages to the EPA Aerometric Information Retrieval System (AIRS), which then performs the 8-hour calculations.

Most agencies already use central processing and polling software that will allow their central computer to do the 8-hour averaging. If not, they should consider requiring the ability to generate 8-hour averages as part of any DAS purchase package. They then will be better able to manipulate their data for their own use.

Ozone concentration can generally be read in *ppm* directly from the instrument's meter or from a properly calibrated recorder. In cases where the recorder scale is not in ppm, a calibration curve is used to correlate the instrument's output value to the pollutant concentration. If it is necessary to convert the concentration to $\mu g/\text{std m}^3$, it can be determined as follows:

(Eq. 6-2)

$$\frac{\mu\text{g O}_3}{\text{std m}^3} = \text{ppm O}_3 \times 1960$$

The constant 1960 relates the molecular volume of ozone at standard temperature and pressure (25ºC, 760 mm Hg) to the concentration of ozone in the sample volume. It is derives as follows:

(Eq. 6-3)

$$\frac{\mu\text{g O}_3}{\text{std m}^3} = \frac{\times\,\mu\text{L}}{\text{L}}\left(\frac{1\times10^3\,\text{L}}{\text{m}^3}\right)\left(\frac{48\mu8}{\mu\text{mole}}\right)\left(\frac{\mu\text{mole}}{24.46\mu\text{L}}\right)$$

$$\frac{\mu\text{g}}{\text{std m}^3} = \frac{\times\,\mu\text{L}}{\text{L}}(1960)$$

where:

$$\text{ppm} = \frac{\mu\text{L}}{\text{L}}$$

QUALITY ASSURANCE AND QUALITY CONTROL

Quality assurance (QA) and quality control (QC) are two terms commonly discussed but often confused. Quality assurance refers to the overall process of ensuring that the data collected meet previously stated measurement quality objectives (MQOs). Quality control covers specific procedures established for obtaining and maintaining data collection within those limits.

Clear communication among all participants is crucial. When all groups perform their jobs correctly and communicate clearly with each other, they form the vital control loop required for any good QA/QC program.

Quality Assurance

There are six commonly used data quality indicators for ozone and other pollutants. Collectively, the first five--precision, accuracy, representativeness, completeness, and comparability-- were once called "PARCC".

Although the term is used less frequently now, it still is a useful designation. The sixth is method detection limit, also called detectibility. Application of each of these terms to ozone measurements is shown in Table 6-4 that summarizes requirements specified in various sections of the *Code of Federal Regulations*, and then discussed in the following sections.

Precision

Precision is defined as the measure of agreement among individual measurements of the same property taken under the same conditions. For ozone, this refers to testing the ozone analyzer in the field at a concentration between 0.080-0.100 ppm. The test must be performed at least once every two weeks, and is used to calculate the 95% probability limits for the data. Precision tests also check for bias, defined as the systematic error in test results. See QA Handbook, Volume II, Part I, Section 6.0, and also Volume I, Section 7, for more details.

Accuracy

Accuracy is defined as the degree of agreement between a measured value and the true, expected, or accepted value. Quantitative comparisons are made between the measured value and the true, standard value during audits. Generally, three upscale points and a zero point are compared. Two audit types commonly used for ozone, direct comparison and blind, are discussed below. The SOP should discuss plans for each type of audit.

1. ***Direct Comparison Audits***: A transfer standard and the monitoring station's ozone analyzer then assay the same ozone concentrations at the same time. The responses of the on-site analyzer are then compared against the output of the transfer standard and a linear regression is generated. See QA Handbook, Volume II, Part I, Appendix A for more details on audit procedures.

2. ***Blind Audits***: In blind audits (also called performance evaluation audits), auditees do not know the ozone concentrations produced by the auditor's equipment. An ozone generator produces ozone concentrations to be measured by the station analyzer. Reponses of the on-site analyzer are then compared against those of the generator and a linear regression is calculated. See QA Handbook, Volume II, Part I, Appendix A, for more details.

Representativeness

Representativeness refers to whether the data collected accurately reflect the conditions being measured. It is the data quality indicator most difficult to quantify. Unless the samples are truly representative, the other indicators are meaningless. Representativeness for ozone is assured, as best as possible, by precise definitions of monitor siting criteria, using several scales: middle, neighborhood, urban, and regional. Siting criteria for ozone monitors are discussed further in the QA Handbook, Volume II, Part I, Sections 6 and 7.

Completeness

Completeness is defined as the amount of data collected compared to a pre-specified target amount. Ideally, 100% of the target amount of data would always be collected; in practice, that value is less for many reasons, ranging from calibration time and site relocation to power outages and equipment failure. For ozone, EPA requires a minimum completeness of 75% (40 CFR 50, App. H.3). Typical completeness values can approach 90-93%.

Comparability

Comparability is defined as the process of collecting data under conditions that are consistent with those used for other data sets of the same pollutant. The goal is to ensure that instruments purchased and operated by states and local agencies produce comparable data. All monitoring agencies must purchase instruments that have been designated by EPA as reference or equivalent methods. See QA Handbook, Volume II, Part I, Sections 6 and 7.3 for additional details.

Method Detection Limit

The method detection limit (MDL) or detectibility refers to the lowest concentration of a substance that can be determined by a given procedure. Because there are several different definitions of MDLs and the resulting values may also differ, any method used for ozone must be able to detect a minimum value of 0.005 ppm of ozone (40 CFR 53.23b). Most instruments do somewhat better than that.

Table 6-4. Data Quality Requirements for Ozone

Requirement	Frequency	Acceptance Criteria	Reference	Information or Action
Precision	Once every 2 weeks	Conc 0.08-0.100 ppm; 95% probability limits within 15% of the mean	40 CFR 58, App. A	If 95% confidence limits fail, implement QC.
Accuracy	SLAMS, once a year PSD, quarterly	Slope: 1.00 +/- 0.15 Intercept: +/- 0.003 ppm Regression: > 0.9950	Part I, Section 18, App. A	Use photometer or generator calibrated against local primary standard or EPA SRP.
Representativeness	--	Dependent on siting criteria	40 CFR 58, App. D	
Completeness	Daily, monthly	SLAMS, 75% PSD, 80%	40 CFR 50, App. H.3 PSD Regulations, EPA 450/4-87-007	
Comparability	--	Must be reference or equivalent method	Part I, Section 7.3	
Method Detection Limit		0.005 ppm	40 CFR 53.23b	

Quality Control

As stated earlier, quality control (QC) refers to procedures established for collecting data within pre-specified tolerance limits. Almost all QC procedures have already been covered under specific topics throughout this guidance document. Documentation and standard operating procedures, however, are discussed below because they apply to many topics.

Documentation

Documentation, unfortunately, is the aspect of a QA/QC program most often slighted. Yet it is even more important for ozone than for other criteria pollutants because there are no locally available NIST standards for ozone. Extensive certification paperwork must be rigorously maintained for each transfer standard, local primary standard, and analyzer, and for verification tests with SRPs or with a local primary standard of other organizations. Monitoring agencies should take special care to prepare and preserve backup copies of all data, especially calibration data. All data and supporting documentation should be held for five years.

Standard Operating Procedures

All agencies and consultants that perform ozone monitoring should develop their own written SOPs tailored to their specific needs and conditions. The SOPs for ozone should include, but are not limited to, the following topics.

- Primary standard verification
- Transfer standard verification
- Ozone analyzer preventive maintenance
- Ozone analyzer operation and scheduling
- Documentation procedures
- Internal audit procedures
- Precision testing
- Data review and validation

Time and effort well spent in preparing SOPs will save far more time and effort in operating the monitoring program.

To assist QA Handbook users in preparing their own SOPs, refer to: *Determination of Ozone by Ultraviolet Analysis, A New Method for Volume II, Ambient Air Specific Methods, Quality Assurance Handbook for Air Pollution Measurement Systems,* Final Draft, May 1, 1997.

HEALTH AND SAFETY WARNINGS

To prevent personal injury, all warnings must immediately precede the applicable step in an SOP. The following warnings should be heeded and any others should be added.

! Ozone is a very strong oxidant. Vent any ozone or calibration span gas to the atmosphere rather than into the shelter or other immediate sampling area. If this is impossible, limit exposure to ozone by getting fresh air every 10 to 15 minutes. If chest tightening occurs, leave the area immediately.

! Ultraviolet light can cause burns to the cornea of the eye. Avoid looking at the UV lamp when it is on. Use protective glasses if the lamp must be checked when it is energized.

! Always use a third ground wire on all instruments.

! Always unplug the analyzer when servicing or replacing parts.

! If it is mandatory to work inside an analyzer while it is in operation, use extreme caution to avoid contact with high voltages inside the analyzer. The analyzer has high voltages in certain parts of the circuitry, including a 220 volt DC power supply, a 110 volt AC power supply, and a start-up lamp voltage of more than 1000 volts. Refer to the manufacturer's instruction manual and know the precise locations of these components before working on the instrument.

! Avoid electrical contact with jewelry. Remove rings, watches, bracelets, and necklaces to prevent electrical burns.

References

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