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-12/531, 2012. This protocol describes 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. Maximum Certification Periods[a] for Calibration Standards in Passivated Aluminum Cylinders

Components	Balance gas	Concentration range	Period (years)
Ammonia	Nitrogen	5 to 50 ppm	1
Carbon dioxide	Air[b]	360 to 420 ppm	8
Carbon dioxide	Nitrogen	5 ppm to 20%	8
Carbon monoxide	Air	40 to 500 ppb	TBD
Carbon monoxide	Air	500 ppb to 10%	8
Carbon monoxide	Nitrogen	1 ppm to 15%	8
Formaldehyde	Nitrogen	0.5 to 10 ppm	1
Hydrogen chloride[c]	Nitrogen	10 to 5000 ppm	2
Hydrogen sulfide	Nitrogen	1 to 1000 ppm	3
Methane	Air	1 to 1000 ppm	8
Methane	Nitrogen	500 ppb to 10%	8
Methanol or ethanol	Nitrogen or Air	75 to 500 ppm	4
Natural gas components[d]	Natural gas	Contact NIST	4
Nitric oxide	O2-free nitrogen[e]	0.5 to 50 ppm	3
Nitric oxide	O2-free nitrogen[e]	50 ppm to 1%	8
Nitrous oxide	Air	300 ppb to 5%	8
Oxides of nitrogen[f]	Air	3 ppm to 1%	3
Oxygen	Nitrogen	10 ppm to 25%	8
Propane	Air	0.1 to 500 ppm	8
Propane	Nitrogen	5 ppb to 2%	8
Sulfur dioxide	Nitrogen	1 to 50 ppm	4
Sulfur dioxide	Nitrogen	50 ppm to 1%-	8
Volatile organics	Nitrogen	1 ppb to 1 ppm	4
Zero air material[g]	Air	Not applicable	Unlimited
Multicomponent mixtures	---	---	See text
Mixtures with lower concentrations	---	---	See text

[a] Specialty gas producers may elect to certify candidate standards for less than the maximum certification period. Each producer has discretion in this matter. See text.
[b] "Air" is defined as a mixture of oxygen and nitrogen where the minimum concentration of oxygen is 10 percent and the concentration of nitrogen is greater than 60 percent.
[c] Hydrogen chloride may be contained in passivated aluminum or nickel-coated steel cylinders.
[d] Natural gas components are methane, ethane, propane, n-butane, iso-butane, n-pentane, isopentane, helium, nitrogen, and carbon dioxide.
[e] O2-free nitrogen contains ≤ 100 ppb of oxygen.
[f] NIST defines its total NOX standards as containing nitrogen dioxide plus contaminant nitric acid.
[g] Concentrations of SO2, NOX, and THC are not >0.1 ppm; concentration of CO is not >1 ppm; and concentration of CO2 is not >400 ppm as per 40 CFR Part 72.2. Zero air material may be contained in steel cylinders.

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.

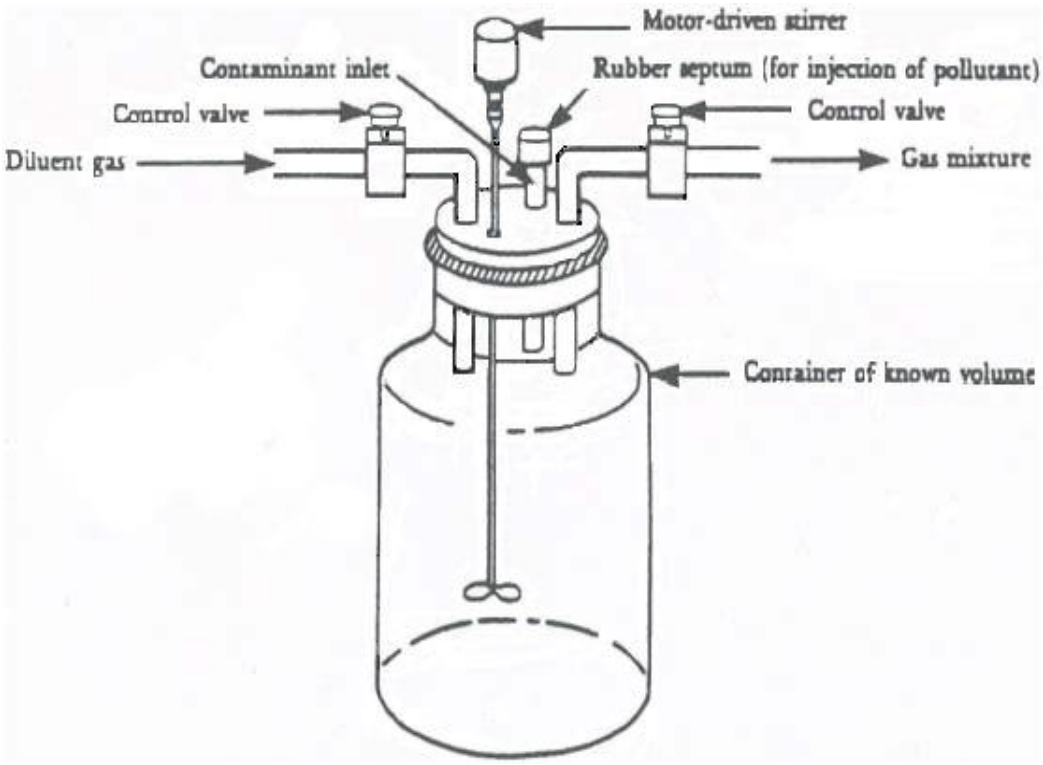


Figure 4-1. Rigid chamber used for producing standard gas mixture.

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

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%):

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

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.

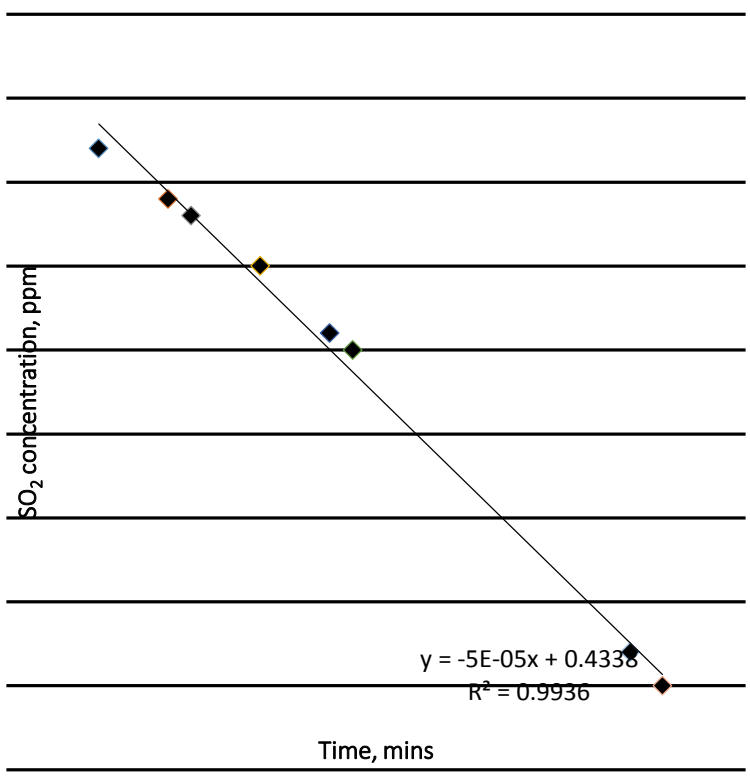


Figure 4-2. Rate if decay of SO2 concentration in a bag.

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, ppm^2	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, ppm^2	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, ppm^2	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. ppm^2	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.

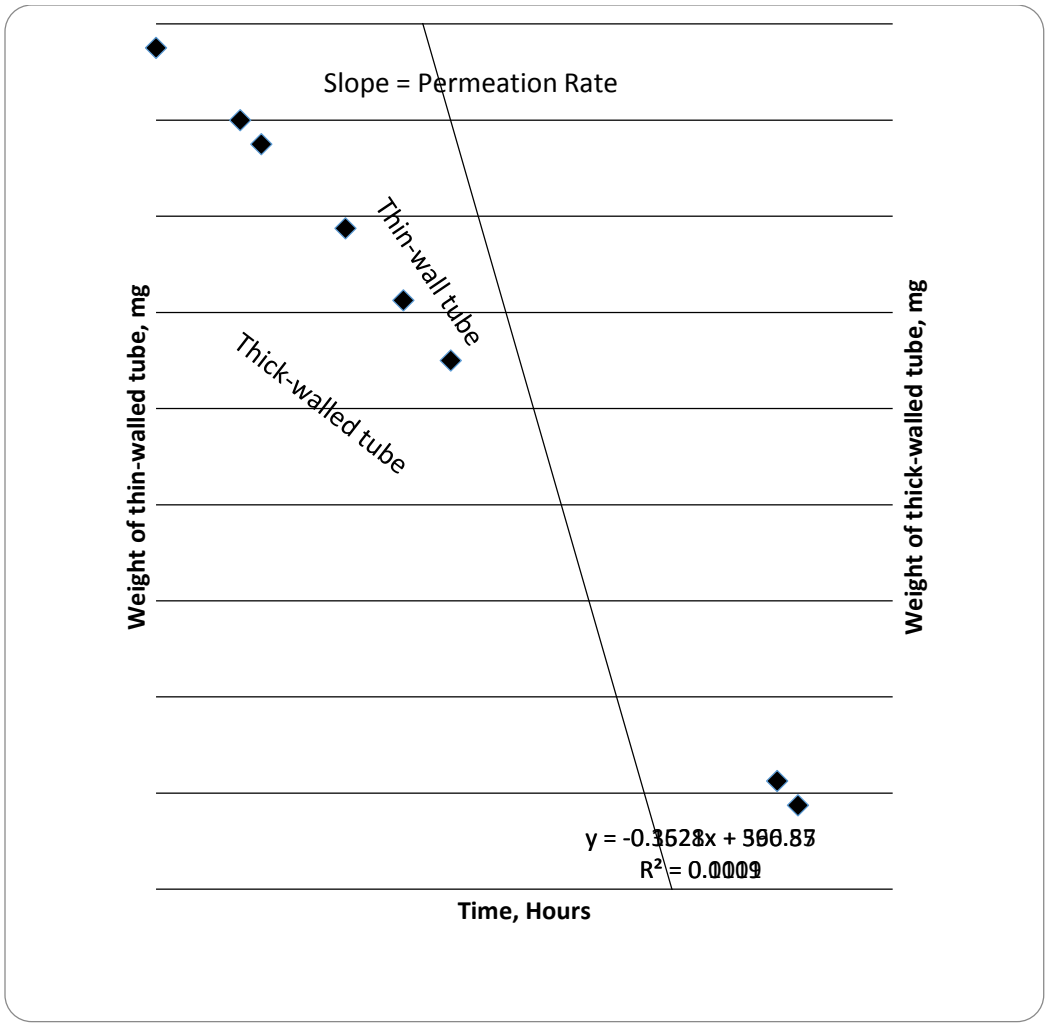


Figure 4-3. Calibration of two permeation tubes.

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.

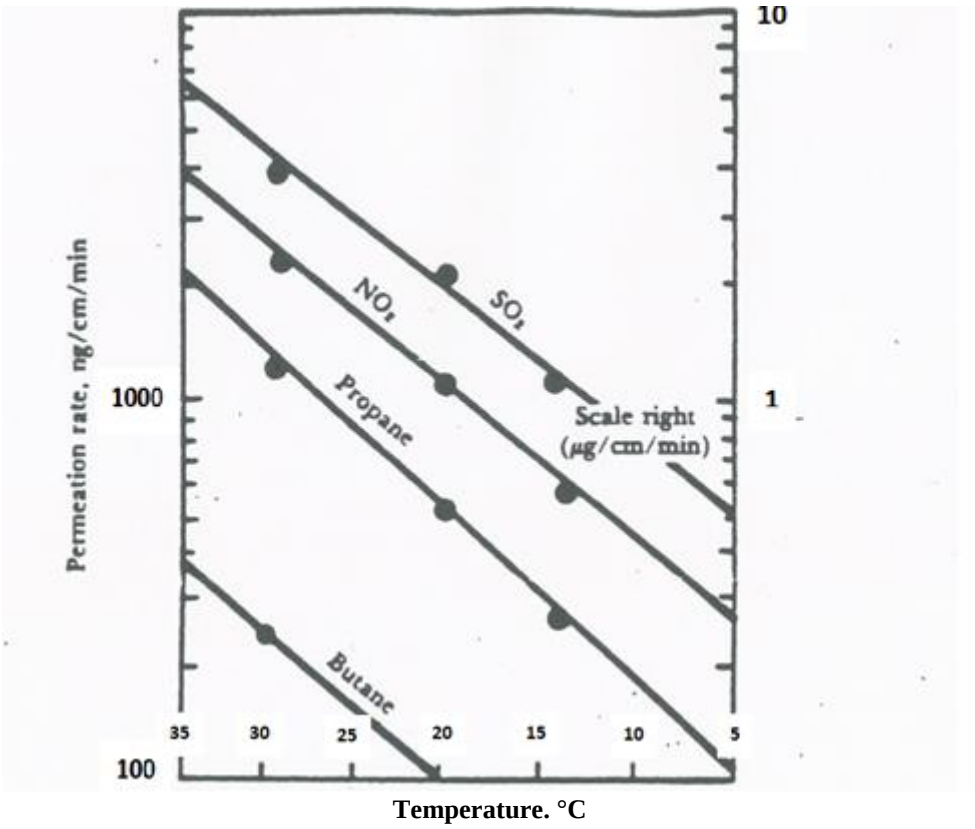


Figure 4-4. Permeation rate vs. temperature for four gases.

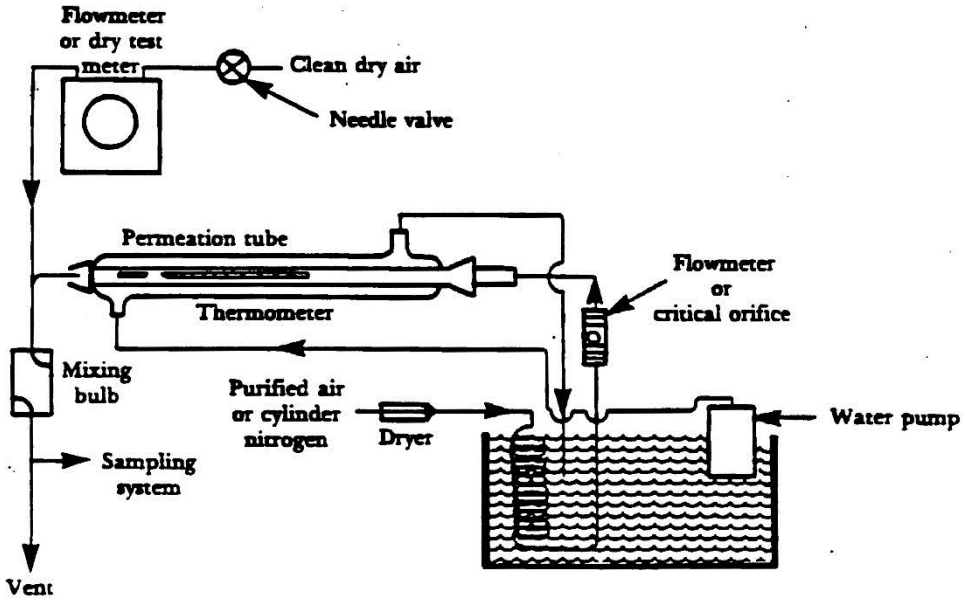


Figure 4-5. Components and flow of a typical permeation system.

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

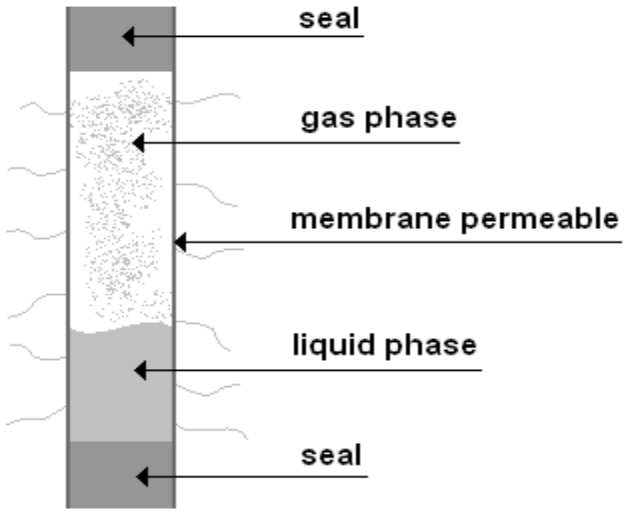
The tubular device, as shown in Figure 4-6, is a sealed permeable cylinder containing the desired permeant gas. Release of the chemical occurs by permeation through the walls of the Teflon® tube for the entire length between the impermeable plugs. A wide range of rates can be achieved by varying the 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.

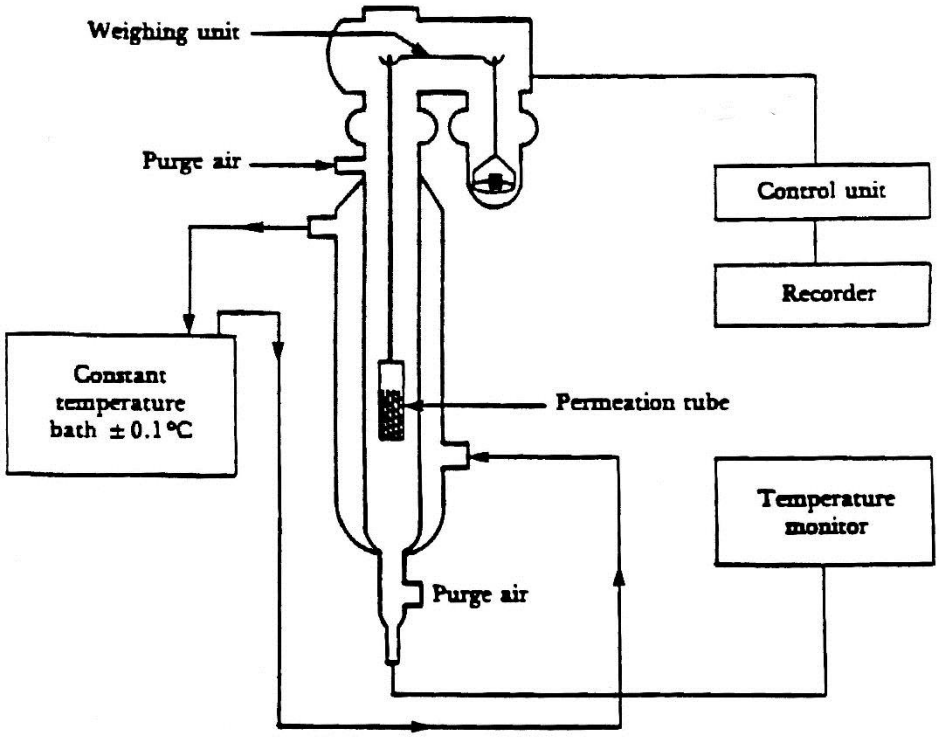


Figure 4-7. Gravimetric calibration apparatus.

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.

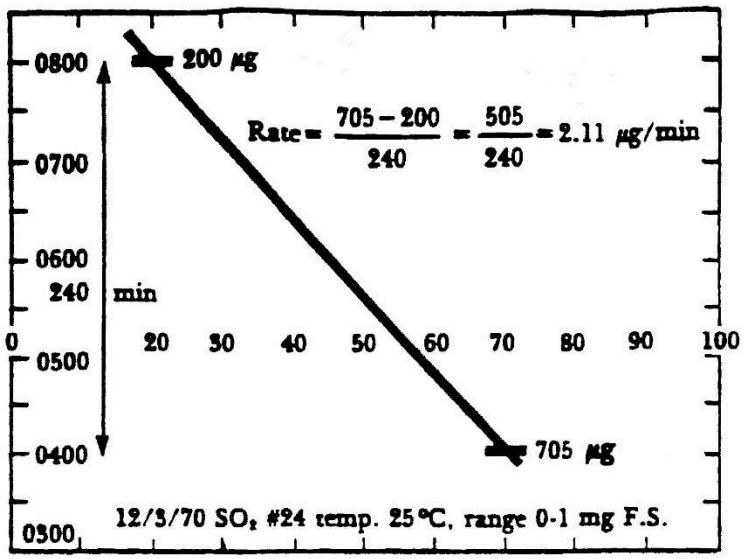


Figure 4-8. Typical strip chart read-out from an in situ thermal-gravimetric apparatus.

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.

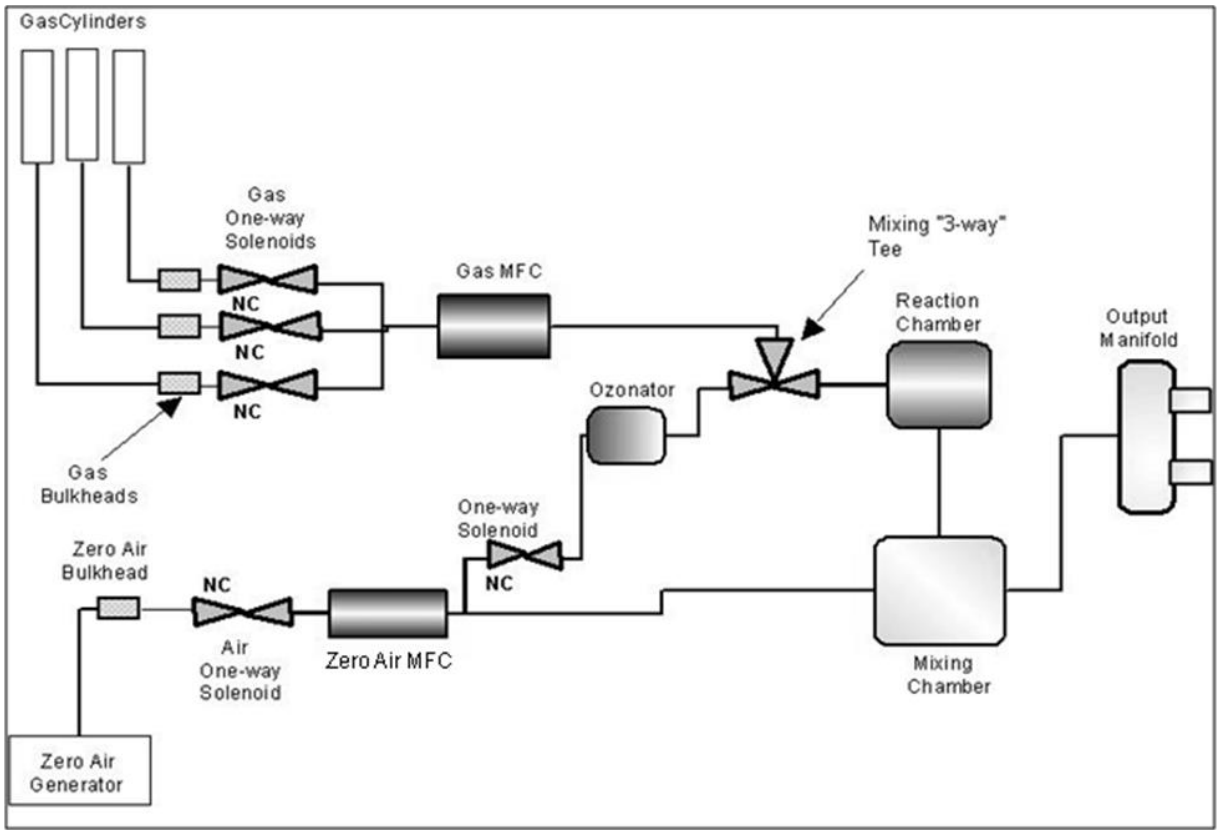


Figure 4-9. Schematic of a typical Multi-gas Dynamic Calibrator equipped with Mass Flow Controllers.

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 be 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 $\pm$ 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

Material	Purpose	Comments
		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.
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., °F	Max. gas Flow, CFH/Ib	Sp. heat, Cp BTU/(lb°R)	Typical adsorbates
Activated carbon	Pellets	10.5-21.5	0.010 -	200 -1000	/	0.25	CH_4 through n-C_6H_{12}
	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 alumina	Beads (G)	7.0-18.5	0.006	350-600	50	0.22	H_2S, SO_2
	Beads (S)	4.0- 8.0		350-1000	50	0.25	Oil vapors
Molecular sieves	Pellets	9.0-14.5	/	300-600	/	0.23	See Tables 6-9 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

Coolant	Temperature, °C
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.

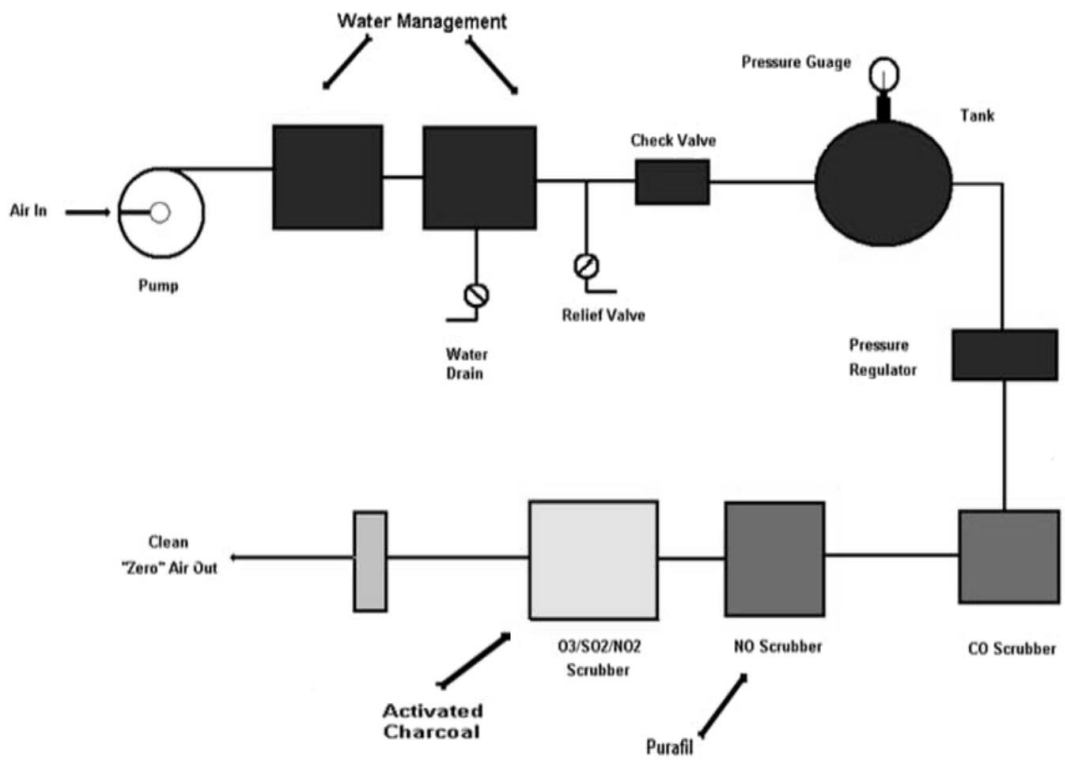
Summary

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^3 (this will actually add very little error). 2.88 x 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):

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

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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