Chapter 11

Gas Sensor Calibration

G as sensors need to be calibrated and periodically checked to ensure sensor accuracy and system integrity. It is important to install stationary sensors in locations where the calibration can be performed easily. The intervals between calibration can be different from sensor to sensor. Generally, the manufacturer of the sensor will recommend a time interval between calibration. However, it is good general practice to check the sensor more closely during the first 30 days after installation. During this period, it is possible to observe how well the sensor is adapting to its new environment.

Also, factors that were not accounted for in the design of the system might surface and can affect the sensor's performance. If the sensor functions properly for 30 continuous days, this provides a good degree of confidence about the installation. Any possible problems can be identified and corrected during this time. Experience indicates that a sensor surviving 30 days after the initial installation will have a good chance of performing its function for the duration expected. Most problems—such as an inappropriate sensor location, interference from other gases, or the loss of sensitivity—will surface during this time.

During the first 30 days, the sensor should be checked weekly. Afterward, a maintenance schedule,

including calibration intervals, should be established. Normally, a monthly calibration is adequate to ensure the effectiveness and sensibility of each sensor; this monthly check will also afford you the opportunity to maintain the system's accuracy.

The method and procedure for calibrating the sensors should be established immediately. The calibration procedure should be simple, straightforward, and easily executed by regular personnel. Calibration here is simply a safety check, unlike laboratory analyzers that require a high degree of accuracy. For area air quality and safety gas monitors, the requirements need to be simple, repeatable, and economical. The procedure should be consistent and traceable. The calibration will be performed in the field where sensors are installed so it can occur in any type environment.

Calibration of the gas sensor involves two steps. First the "zero" must be set and then the "span" must be calibrated.

Step One: Setting the "Zero" Reading

There is no established standard that defines zero air. Many analytical procedures, including some specific analyzer procedures such as EPA methods, use pure nitrogen or pure synthetic air to establish the zero point. The reason for this is that bottled nitrogen and pure synthetic air are readily available. As a result, it is popularly believed that using bottled nitrogen or synthetic air is a good method to zero a sensor.

Unfortunately, this is not correct. Normal air contains traces of different gases besides nitrogen and oxygen. Also, ambient air normally contains a small percentage of water vapor. Therefore, it is much more realistic and practical to zero the sensor using the air surrounding the sensor when the area is considered to be clean. This reference point can be difficult to establish. Therefore, a good reference point

can be in the area where air is always considered clean, such as in an office area. This will give a more realistic representation of the zero point because it will be representative of the local ambient air condition. The lack of water vapor can cause the zero point setting to read lower than in ambient air making the sensor zero appear to drift. This is most noticeable in solid-state sensors and PIDs.

Calibration Methods. Taking all factors such as the type of sensor and the conditions of the application into consideration, the following are some proposed methods of calibration:

A. In applications where the ambient air is normally clean, and, based on the operator's judgment that no abnormal condition exists and the instrument is indicating a close to zero reading, the procedure to zero the sensor can be skipped. When in doubt, use a plastic bag to get a sample of what is considered to be "clean air" in the facility and expose it to the sensor for a few minutes. This is a very quick and easy procedure. It is also a very effective way to differentiate a real alarm from a false alarm.

B. Compressed air has the advantage that it is easy to regulate and can be carried around in a bottle. Also, in many facilities, shop air is available throughout the plant, making it very accessible and convenient. However, most shop air contains small concentrations of hydrocarbons, carbon monoxide, carbon dioxide, and possibly other interference gases. Also, the air is typically very low in humidity. A solution to this is that the air can be filtered through activated charcoal to remove most of the unwanted gases and water vapor can be added into the air using a humidifier in the sampling system. After this conditioning, the air can be used to calibrate most types of sensors. However, it is important to note that carbon monoxide is *not* removed by charcoal filters.

It is therefore imperative to make sure that the
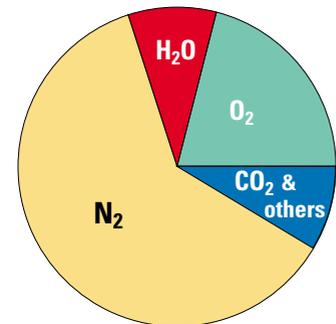
Ambient air is the best zero air.

CO concentration in the shop air is the same as in the ambient air. Furthermore, a soda ash filter should be used to remove carbon dioxide. This is also a very good way to zero carbon dioxide sensors since placing a soda ash filter in-line with the sampling system will remove all carbon dioxide, thus providing an easily obtainable zero baseline.

Although synthetic air is usually very pure, it cannot be used with solid-state sensors or PID sensors because these sensors require some water vapor in the sample stream. A simple solution to this problem is to add a wet tissue paper in the sample line. This acts as a humidifier in the sample stream and provides enough water vapor for the sensor to read properly. Another option is to use a Nafion tube, which is described thoroughly in Chapter 10, "Sampling Systems and Designs." Figure 1 illustrates this concept.
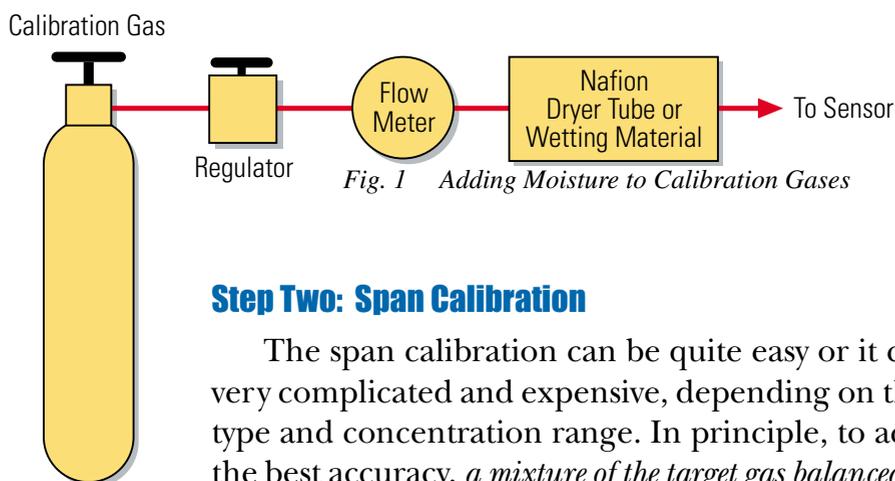
Calibration Gas

Regulator

Fig. 1   Adding Moisture to Calibration Gases

Step Two: Span Calibration

The span calibration can be quite easy or it can be very complicated and expensive, depending on the gas type and concentration range. In principle, to achieve the best accuracy, *a mixture of the target gas balanced in the background environmental air is the best calibration gas.* However, although this can be done, it usually requires that the operators be more skilled than would usually be required. In practice, most calibration gases are purchased from commercial suppliers. The following section describes a few methods of span calibration.

A. Premixed Calibration Gas

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This is the preferred and most popular way to calibrate gas sensors. Premixed gas mixtures are compressed and stored under pressure in a gas bottle. The bottles are available in many sizes but most field calibrators employ smaller, lightweight bottles. These small portable bottles come in two different categories: a low-pressure and a high-pressure version.

The low-pressure bottles are thin-walled, lightweight bottles that are usually nonreturnable and disposable. High-pressure bottles are designed to bottle pure hazardous chemicals. For calibration gases, these bottles are normally made of thick-walled aluminum which has a service pressure of 2000 psi.

To get this highly pressurized gas out of the bottle in order to calibrate the sensor, a regulator assembly is needed. This assembly consists of a pressure regulator, a pressure gauge, and an orifice flow restrictor. The orifice flow restrictor is a fitting with a hairline hole that allows a constant air flow at a given pressure difference. In operation, the high pressure from the bottle is reduced to a lower pressure of only a few psi, which provides a constant air flow through the orifice. Flow rates between 600-1000 cc/min are most common. Models can be fitted with an adjustable pressure regulator so that the flow rate can be adjusted accordingly. Figure 2 illustrates typical models of high- and low-pressure bottle assembly.

Many gases can be premixed with air and stored under pressure, but some gases can only be mixed in inert gas backgrounds, such as nitrogen. Some mixtures can only be stored in bottles that are specially treated or conditioned. Each type of mixture will have a different amount of time before it expires or before it can no longer be used.

Low-Pressure Assembly   High-Pressure Assembly

Fig. 2   Calibration Gas Bottles

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Detailed information about storage and shelf life can be obtained from the manufacturer. Generally, high vapor pressure gases with low reactivity, such as methane, carbon monoxide and carbon dioxide, can be mixed with air and stored under high pressure. Low vapor pressure gases, such as liquid hydrocarbon solvents, can only be mixed with air and stored under low pressure. Most highly reactive chemicals are mixed with a nitrogen background. With certain sensors, such as solid-state sensors, whether the mixture of the gas is in the air or in the nitrogen background will dramatically affect the sensor reading.

During calibration, some sensors may need moisture to get a proper reading. Moisture can be added by following the same procedure described in Step 1 for zeroing the sensor.

To estimate the volume of a pressurized gas in a cylinder, take the total pressure (P) divided by the atmospheric pressure (P_a) and multiply this ratio by the volume of the cylinder:

$$V_{mix} = V \cdot (P/P_a)$$

where

    V_{mix} = the volume of the gas mixture
    V   = the volume of the cylinder
    P   = the pressure in the cylinder
    P_a = the atmospheric pressure

For example, let's say a given lecture bottle has a 440 cc volume (V). Assume the bottle has a 1200 psi pressure. The estimated volume of the premixed gas at atmospheric pressure is: (440 cc) x (1200/14.7) = 35,918 cc.

If the flow rate of the calibration gas is 1000 cc per minute and it takes approximately one minute per sensor to calibrate, a single cylinder can be used to calibrate approximately 30 times.

B. Permeation Devices

A *permeation device* is a sealed container that contains chemicals in liquid and vapor phase equilibrium. The gas molecules are either permeated through the permeable container wall or through the end cap. The rate in which the gas molecules permeate depends on the permeability of the material and temperature. The rate of permeation is constant over long periods of time. At a known rate of permeation at a given temperature, a constant flow rate of air mixed with the permeated chemicals forms a constant stream of calibration gas. A calibrator with constant temperature and flow regulation is needed. However, the permeation tube continuously emits chemicals at a constant rate thus creating a storage and safety problem. Also, the rate of permeation for a given gas of interest can be too high or too low for a given application. For example, high vapor pressure gases permeate too quickly while very low vapor pressure chemicals have a permeation rate that is too low to be of any use.

Examples of Permeation Tubes

Permeation devices find most of their use in laboratories and in applications using analytical analyzers. For gas monitoring applications, the concentrations needed to calibrate the sensor are typically too high for the permeation device. Therefore, they have been found to be of limited use.

C. Cross Calibration

Cross calibration takes advantage of the fact that every sensor is subject to interference by other gases. For example, for a sensor calibrated to 100% LEL hexane, it is usually much easier to use 50% LEL *methane* gas to calibrate the sensor instead of using an actual hexane mixture. This is because hexane is a liquid at room temperature and it has a low vapor pressure. Therefore, it is more difficult to make an accurate mixture and to keep it under high pressure.

On the other hand, methane has a very high vapor pressure and is very stable. Furthermore, it can be mixed with air and still be kept under high pressure. It can be used for many more calibrations than a hexane mixture in the same size bottle and it has a long shelf life. A 50% LEL methane mixture is also readily available. Therefore, it is common practice for manufacturers of combustible gas instruments to recommend the use of methane as a substitute to calibrate for other gases.

There are two ways to accomplished this task. The first method is to calibrate the instrument to methane while other gas readings are obtained by multiplying the methane reading by response factors that are included in the manual. This is commonly done with catalytic sensors. Catalytic sensors have a linear output and therefore the use of this response factor is applicable to the full-scale range. For example, pentane has an output of only half that of methane gas when the sensor is calibrated to methane. Therefore, it has a response factor of 0.5. So, if the instrument is calibrated to methane but is used to measure pentane, the reading is multiplied by 0.5 to obtain the pentane reading.

The second method is to still use methane as the calibration gas, but double the value of the reading of the calibration. For instance, use 50% LEL methane calibration gas and calibrate with this as 100% LEL pentane. After the calibration, the instrument directly indicates the pentane gas concentration although it was calibrated using methane gas.

Many low-range toxic gas sensors can be calibrated using cross gas calibration. Also, with infrared instruments, any gas within the same wavelength of absorption can be used for cross calibration. The advantage of cross calibration is that it allows the sensor to be calibrated with a gas and range that is easier to obtain and handle.

However, there are some problems with using cross calibration. One is that the response factors for each sensor can be different as it is generally impossible to make most sensors exactly alike. For example, in catalytic sensors, the heater voltage has to be as specified in the manual; otherwise, the response factor will not be applicable. The response characteristics will vary with different heater voltage settings. Therefore, it is a good practice to periodically check the calibration of the sensor with the actual target gas.

Mixtures of stable noncombustible and nontoxic gases with various concentrations are available from many supply sources. Check with the instrument manufacturer for more detailed information.

D. Gas Mixing

Not all calibration gases are available. Even if they are available, it is very possible that they would not be available in the right concentration or in the proper background mixture. However, many mixtures are available for some process uses which can be diluted to use in calibration of gas monitors in lower concentration ranges. For example, 50% LEL methane has a concentration of 2.5% or 25,000 ppm. To make a 20% LEL mixture having a volume of 2000 cc, the following formula can be used:

$$V_b = \frac{C}{C_b} \cdot V, \qquad V_a = \frac{C - C_b}{C} \cdot V$$

and

$$V_a = V - V_b$$

where

C_b = concentration in the bottle, 50% in this case

C = new concentration, 20% in this case

V = total final volume, 2000 cc in this case

V_b = volume of mixture

V_a = volume of air or other dilutant

$$V_b = 20/50 \cdot 2000 = 800 \text{ cc}$$

$$V_a = 2000 - 800 = 1200 \text{ cc}$$

The final mixture would be made by taking 800 cc of the calibration gas and mixing it with 1200 cc of air to make the mixture equal to 20% LEL.

Another example is to dilute this 25000 ppm of methane calibration gas to make a 100 ppm of mixture.

$$V_b = 100/25000 \cdot 2000 = 8 \text{ cc}$$

therefore

$$V_a = 2000 - 8 = 1992 \text{ cc}$$

By mixing 8 cc of calibration gas into 1992 cc of air, 2000 cubic centimeters of 100 ppm gas mixture is obtained.

Some Calibration Tools

To perform the above procedure, the following tools are needed:

A 2"-Diameter, 1000 cc Syringe

1. *Syringe and Needle:* This is the most inexpensive way to accurately measure the amount of gas. A disposable medical syringe with a large gage needle is most practical but there are few syringes with more than one hundred cubic centimeter volume. Hence, large volume measurements can be troublesome. However, it is easy to make a syringe using any standard size pipe having about a 2-inch diameter. It provides an easy and convenient means to make a mixture on a regular basis. For very small volume measurements, there are micro syringes that are readily available in chemical supply catalogues.

Standard Medical Syringes:
1 cc, 10 cc, and 50 cc

2. *Calibration Bag:* Most of the materials used in food packaging or storage are quite inert; otherwise, food would be contaminated with odor. Therefore,

food storage bags can be used to hold most chemicals as long as they are used for relatively short durations. This is an important point to keep in mind since gas molecules will eventually diffuse through the many thin layers of a plastic bag. For example, potato chips can stay fresh in their original bag for long periods of time because the bag material is less permeable by gas molecules than normal food storage bags. This is demonstrated by the fact that when the potato chips are transferred into a tightly sealed food container bag, they will lose their crispness in a very short time. There are also many commercially available sampling bags on the market. One common example is a Tedlar bag. It is made from polyvinyl fluoride and has low absorption of gas molecules. However, this type of bag is still permeable, so a heavy gauge material will be needed if permeability is a major concern. Sampling bags normally come with a valve and a septum that is used as an injection port.

A 5-liter Sampling Bag

Pressure Formula

Earlier, we described preparing a mixture based on a volume relationship. Based on the ideal gas law, the same volume formula can be used as a *pressure formula.* As an illustration, take an 800 psi mixture of 50%LEL methane with a 1200 psi mixture of air. This will result in a 2000 psi mixture of 20%LEL methane.

Preparing gas mixtures can be a very difficult task. It is best to consult with the instrument manufacturer regarding the best method of calibration and availability of gas mixtures.

1000 cc Calibration Cans

Following are some examples of how gas mixtures can be made:

For ppm gas mixtures:

$$C_{ppm} = V_c / (V_c + V_d) \cdot 10^6 \, ppm$$

where V_c is target gas volume and V_d is the

Mixing Calibration Gas

dilutant volume. For example, what is the concentration in parts per million when 1 cc of CO is added to a 1000 cc container?

$$C_{ppm} = 1/1000 \cdot 10^6 = 1000 \text{ ppm}$$

For % range gas mixtures:

$$C_{\%} = V_c/(V_c + V_d) \cdot 10^2 \%$$

The V_c term in the denominator can be insignificant in low ppm mixtures.

Calibrating Liquid Chemical Mixtures. To make a calibration mixture for liquid chemicals, a known volume of liquid is vaporized in a known volume of dilutant air. The ideal gas law states that one gram mole of molecules will occupy 24,500 cc of volume at 25 degree centigrade and at 760 mm of mercury or sea level atmospheric pressure. This temperature and pressure is also called the *standard condition.* At standard conditions, the equation is:

$$C_{ppm} = 24.5 \cdot 10^9 \cdot (V \times D)/(V_a \cdot M)$$

where V = volume of liquid, D = density of the liquid, which is the same as the specific gravity, V_a = the volume of the dilutant air, and M = the molecular weight of the liquid.

Since it is easier to measure the liquid using a micro syringe, the equation then becomes

$$V = C_{ppm} \cdot V_a \cdot M/(24.5 \cdot 10^9 \cdot D)$$

where all units are in milliliters, cubic centimeters, and grams.

For example, benzene has M = 78.1 g and D = 0.88 g/cc. What is the amount of benzene needed to make a 1000 ppm mixture in a 2000 cc bottle?

$$V = 1000 \cdot 2000 \cdot 78.1/(24.5 \cdot 10^9 \cdot 0.88)$$

which yields

$$V = 7.2 \cdot 10^{-3} = 0.0072 \text{ cc} = 7.2 \text{ microliters}$$

Many containers are sized by gallons. Therefore, it is useful to know that *one gallon is equal to 3785 cc.*

Ventilation Hood for Calibration Procedures

In air pollution, industrial hygiene, and medical toxicology work, the commonly used unit of concentration is milligram per cubic meter. The following equation expresses this relation, again assuming standard conditions.

$$C_{ppm} = C \cdot 24.5/M$$

where

C = mg/m^3
M = molecular weight

In conclusion, for the calibration of gas monitors, accuracy is not extremely important because these are not analytical devices or systems. *However, it is most important to keep the calibration methods standardized and easily traceable.* If procedures are standardized, data can be normalized at a later date if necessary.