MEASURING GASEOUS POLLUTANTS FROM DIESEL EXHAUST IN UNDERGROUND MINES

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ABSTRACT

Several techniques are available today for measuring gaseous pollutants from diesel exhaust such as carbon monoxide, carbon dioxide, nitric oxide, nitrogen dioxide, and sulfur dioxide. Four gas-sensing techniques are discussed: electrochemical, infrared, detector tubes, and passive samplers. For each technique, the general operating principles are described, and a discussion of measurement range, response time, accuracy, interferences, power requirements, life, and cost is included. Selecting the most appropriate technique is challenging. Each of the four techniques have benefits and shortcomings that must be evaluated in light of the sampling objective. At present, no "recommended" sampling or measurement protocol is available. A complete discussion of the problem of measuring gases present in diesel exhaust would require several large volumes. This paper is intended as an introduction to the problem.

INTRODUCTION

Exhaust from diesel equipment used in mines contains a wide variety of pollutants, both gaseous and particulate in nature. The health implications and related industrial hygiene issues arising from the use of diesel equipment are discussed in another paper in this Information Circular (IC). Measurement of particulate pollutants will also be discussed elsewhere in this IC. This paper will discuss measurement techniques and instruments for measuring gaseous pollutants from diesel exhaust, including carbon monoxide (CO), carbon dioxide (CO_2), nitric oxide (NO), nitrogen dioxide (NO_2), and sulfur dioxide (SO_2).

Four gas-sensing techniques will be discussed: electrochemical, infrared, detector tubes, and passive sampler tubes. For each technique, the general operating principles will be described, and then a discussion of measurement range, response time, accuracy, interferences, power requirements, life, and cost will be included.

This paper will not attempt to provide a buying guide by listing every available monitor suitable for measurement in underground mines and discussing specific features. Rather, the text will review commonly used sensing technologies and the associated benefits and pitfalls of each.

Reports that discuss specific equipment and list manufacturers for measuring diesel exhaust gases can be found in the literature (*1-3*).[5] Other reports list gas measuring equipment that has been approved by the Mine Safety and Health Administration (MSHA) for operation in gassy mines (*4*).

MEASUREMENT CONSIDERATIONS

A myriad of instruments exist on the market today for measuring diesel exhaust gases. However, a necessary first step in any data-gathering episode is to develop some type of monitoring strategy. Examples of possible objectives are determining average exposure of workers to a particular contaminant, alarming workers to an imminent hazard, monitoring the performance of a diesel engine or of a contaminant control system, collecting exposure data for use in epidemiological studies, etc.

Selecting an objective leads to important questions about the way data are collected. For example, will the average of several intermittent grab samples supply the information that is needed, or is the time-resolved history of continuous sampling necessary? Is immediate indication of

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contaminant levels necessary (perhaps even an alarm), or can the data be analyzed remotely at a later time? Should samplers be attached to or carried by each individual worker, or can they be placed at an appropriate location at the work site?

The answers to these questions, as well as other considerations such as the ruggedness and explosiveness of the environment or the range of contaminant levels that could be encountered, comprise the sampling protocol. The protocol in turn makes certain requirements that help determine the appropriateness of particular sampling-measurement devices. Developing monitoring strategies is beyond the scope of this paper; however, a detailed scheme for developing a monitoring strategy for air contaminants from diesel exhaust was formulated in 1983 by the Rocky Mountain Center for Occupational and Environmental Health (*5*). This reference also contains a helpful review and summary of measurement methods, and an extensive bibliography on the subject of diesel pollutant health issues and measurement methods.

ELECTROCHEMICAL

An electrochemical gas cell consists of at least two electrodes that are in contact with an electrolyte. Electrodes are solid electrical conductors that allow electric current to enter and leave an electrolyte. The electrolyte is a substance (either liquid or solid) that dissociates into negatively and positively charged ions.

Electrochemical cells exist in a variety of configurations; however, figure 1 illustrates features that are common to most. This illustration shows the sensing electrode (also referred to as an active or working electrode), a counter electrode, and a reference electrode.

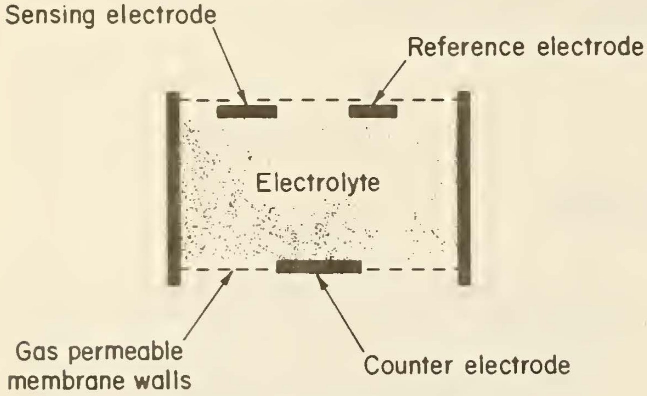

Figure 1.—Electrochemical cell.

To operate the cell, an external electrical potential is applied across the sensing and counter electrodes. The voltage between the reference electrode and the sensing electrode is maintained constant by an appropriate power supply and control circuit. The gas to be measured must be allowed to contact the sensing electrode. This contact is often accomplished by a porous membrane that allows the gas to pass through to the electrode while preventing the electrolyte from leaking out of the cell. A chemical reaction takes place at the sensing electrode that produces electrons that move through the electric circuit and ions that are free to move through the electrolyte. Because of the electric potential imposed between the electrodes, charged ions flow through the electrolyte from one electrode to the other. The number of electrons created by the reaction is proportional to the concentration of gas passing through the membrane. This current is measured and displayed on a meter as gas concentration in engineering units.

When designing an electrochemical cell to detect a certain gas, the manufacturer must select appropriate materials for the electrodes, electrolyte, and porous membrane, and must apply the appropriate voltage to the electrodes to allow the ion flow to take place. As an example, consider a typical CO electrochemical cell. Design parameters must be selected so that CO diffusing to the sensing electrode (anode) reacts with water in the electrolyte according to

$$CO + H_2O = CO_2 + 2H^+ + 2e^-. \qquad (1)$$

At the counter electrode the reaction is

$$\tfrac{1}{2}\, O_2 + 2H^+ + 2e^- = H_2O. \qquad (2)$$

The oxygen required for the reaction in equation 2 is supplied from the ambient air by diffusion to the cell.

In the reaction with CO described here, the sensing electrode served as an oxidizing electrode where CO was oxidized to CO_2. A sensing electrode can also be used as a reduction electrode,[6] as in the case of an electrochemical NO_2 cell. Details of numerous electrochemical gas sensing instruments are available throughout the literature (*6-8*). Numerous patents are now held for designs of electrochemical CO, CO_2, NO, NO_2, and SO_2 gas detecting sensors (*9-10*).

RANGE

Any discussion of the measurement range of mine gas instruments would be meaningless without information about typically expected gas concentration levels. In that context, several terms shall be defined. Table 1 lists threshold limit values (TLV's) (*11*) or exposure standards for CO, CO_2, NO, NO_2, and SO_2. TWA means time weighted average and refers to the maximum allowable average gas level over an 8-h working shift. STEL means short-term exposure level and refers to the maximum allowable average gas level over a 15-min period. IDLH (*12*) refers to the gas level that is immediately dangerous to life or health; that is, the maximum gas concentration from which a person can escape within 30 min without any escape-impairing symptoms or irreversible health effects. Table 2 lists gas

Table 1.— TLV exposure standards, parts per million

Gas	TWA	STEL	IDLH
CO	50	400	1,500
CO_2	5,000	30,000	50,000
NO	25	[1]35	100
NO_2	3	5	50
SO_2	2	5	100

[1] Value for 1985-86; deleted in table for 1986-87 (*11*).

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[6] Typical chemical reactions in electrochemical cells are given at the end of this paper.

Table 2.—Typical diesel exhaust gas concentrations in mines, parts per million

Gas	Diesel exhaust	Diluted exhaust in mine atmosphere
CO	200- 2,500	10 - 20
CO_2	8,000-10,000	1,000 -5,000
NO	500- 1,000	2 - 10
NO_2	12- 20	.5- 1
SO_2	NA	NA

NA Not available.

concentrations representative of those that have been measured by Bureau of Mines researchers in diesel engine exhaust and in the atmospheres of underground mines downstream from diesel equipment.

Electrochemical sensors capable of detecting CO, CO_2, NO, NO_2, and SO_2 have been developed and at least one commercial instrument using electrochemical cells exists for each gas. The measurement ranges listed in table 3 for each of the five gases were compiled from manufacturers' specification literature and are typical of commercial electrochemical gas instruments; however, instruments with higher or lower measurement ranges are also available. To measure these gases at the tailpipe with such monitors, dilution may be required. In general, electrochemical gas monitors are available with measurement ranges adequate for monitoring CO, CO_2, NO, NO_2, and SO_2 in underground mines that use diesel equipment.

Table 3.—Typical measurement ranges for electrochemical gas monitors, parts per million

Sensor type	
CO	0- 2,000
CO_2	0-10,000
NO	0- 1,000
NO_2	0- 100
SO_2	0- 100

RESPONSE TIME

The response time of a gas instrument is usually defined as the time required for the instrument to reach 90 pct of its final reading when challenged with a step change in gas concentration. According to most manufacturers, the response time for diffusion-type electrochemical gas monitors is typically less than 2 min. This information is important only when compared to the expected magnitude and rate of change of gas concentration and to the time required for the concentration of gas being measured to cause harm to those exposed. Consider, for example, a sudden exposure to 5 pct CO. At such levels, unconsciousness and death can occur within minutes. Obviously, any monitor used to alert workers to this situation must have a very short alarm time.

On the other hand, table 2 indicates that typical gas levels in underground mines that use diesel equipment with adequate ventilation are far below levels that would pose immediate hazards to workers. In that case, the response time of electrochemical gas monitors will be adequate for measuring gas concentrations that normally result from the use of diesels in underground mines.

ACCURACY

As discussed earlier, electrochemical sensors produce an electrical signal proportional to the amount of gas available for the chemical reaction. That electrical signal is amplified and used to operate a meter that indicates gas concentration in engineering units. Electrochemical gas monitors can be calibrated by exposing them to a known concentration of gas and then adjusting the gain of the amplifier circuit so that the meter indicates the concentration of the challenge gas. To calibrate electrochemical instruments underground, supplies of stable gases at the concentration levels of interest must be used. Such gases are available in small metal cylinders for CO in air, CO_2 in air, and NO in nitrogen. On the other hand, sufficiently low concentration mixtures of NO_2 and SO_2 (2 to 5 ppm) are generally not available in such cylinders, making field calibration difficult. Laboratory calibration of NO_2 and SO_2 instruments can be accomplished, however, using accurate, low-concentration mixtures obtained from a permeation tube system.

Because of certain changes in the electrochemical cell when used, or simply because of aging, electrochemical gas monitors must be periodically recalibrated. Environmental factors such as changes in temperature and barometric pressure can also affect the accuracy of electrochemical gas sensors. Manufacturers normally incorporate some means of compensating for variations in temperature. A calibration period of once every 30 days of operation is required by MSHA for underground fixed-point carbon monoxide monitors (*13*). Once calibrated, however, typical accuracy cited by manufacturers of electrochemical gas monitors is ±2 pct of the reading. Typical sensor output drift is less than 2 pct of full scale per month.

INTERFERENTS OR CROSS-SENSITIVITY

Occasionally, other gases present in the atmosphere can enter into the chemical reaction and either enhance or diminish the electrical signal produced. These gases are called interferents. For example, according to the manufacturer's specification literature for a particular commercial electrochemical CO monitor, 100 ppm of hydrogen (H_2) will cause the monitor to indicate 30 ppm of CO. If 10 ppm of CO is present with the 100 ppm of H_2, the monitor will indicate a total of 40 ppm CO. This positive interference causes falsely high readings of CO, possibly resulting in false alarms. On the other hand, 10 ppm of NO_2 will cause the monitor to indicate −6 ppm CO. This negative interference results in falsely low readings of CO. In this case, workers may unknowingly be exposed to excessive levels of CO. Table 4 was compiled from specification literature from various manufacturers and lists common interferents for CO, CO_2, NO, NO_2, and SO_2 electrochemical sensors that could be found in underground mines that use diesel equipment. In some cases, interferents can be removed by chemical filters that allow only the gas of interest to reach the sensor. Fortunately, NO and NO_2, common pollutants in diesel exhaust and interferents for electrochemical CO sensors, as well as ethylene and hydrogen sulfide are easily removed by chemical filters. On the other hand, H_2 cannot

Table 4.—Interferents possibly found in underground mines for electrochemical sensors

Sensor type	
CO	H_2, C_2H_2, C_2H_4, NO, NO_2, H_2S, SO_2.
CO_2	SO_2.
NO	H_2S, NO_2.
NO_2	SO_2.
SO_2	H_2S, NO_2.

be removed by any known chemical filter. Thus if CO measurements must be made in the presence of hydrogen, a falsely high reading could result. Furthermore, some chemical filters become less effective with use. Before purchasing any electrochemical instrument, prospective buyers are strongly urged to consult manufacturers for specific information about interferents and the effectiveness of filters that might be incorporated.

POWER

Most electrochemical cells require very little current (typically a few microamperes) and very little voltage (4 V or less). Control circuitry, amplification of signals, etc., would require additional power. Such low-current, low-power electrochemical gas sensing cells are incorporated in battery-operated, handheld, and portable instruments as well as larger, ac-powered monitors intended for operation at fixed monitoring sites. Many of the battery-operated instruments are designed to be intrinsically safe for use in explosive methane-air mixtures found in underground coal mines.

LIFE

Most portable and handheld electrochemical gas monitors are warranted for 1 yr. In practice, however, operating life of CO, NO, NO_2, and SO_2 sensors is expected to be 1 to 2 yr.

COST

Handheld electrochemical gas instruments typically range from $500 to $1,000. Portable monitors intended for monitoring at a fixed location may cost up to $2,000, depending in part on the measurement range and whether more than one measurement range is included. Annual sensor replacement costs can range from $100 to $300 per instrument. Batteries usually need replacement semiannually, and some additional costs will be incurred for calibration equipment and standard tank gas replacement.

INFRARED

Light is comprised of radiation over a wide range of wavelengths. All materials, including gases from most chemical groups, are capable of absorbing certain wavelengths of light. If infrared light (say from 2.5- to 15-μm wavelength) is passed through a gas, light of specific wavelengths within that range will be absorbed.[7] If one measures and graphs the intensity of light passing through a gas versus the wavelengths, the wavelengths at which light is absorbed will be apparent. This graph of peaks and valleys is referred to as an absorption spectrum. The specific wavelengths of light that a substance absorbs depend on the particular construction of its molecules. The energy of infrared light absorbed by a gas causes increases in molecular vibration or rotation. Simple compounds such as CO, CO_2, NO, NO_2, and SO_2 have simple absorption spectra, each with a few pronounced valleys at wavelengths where the greatest absorptions occur. These valleys are called absorption wavelengths or absorption bands. The spectra are simple because the molecules themselves have simple structures.

To measure the airborne presence of any of the preceding gases, one must identify a convenient absorption band in its infrared spectrum, that is, a wavelength of infrared light that is absorbed. However, more is involved in building an infrared detection system than making a choice on the wavelength to be used. Care must be taken that no other airborne gas or material in the light path absorbs the wavelength of interest to any substantial degree. If such an additional absorption occurs, the detection system will respond to the presence of the secondary material as well as the gas one intends to measure. This obscuring, overlapping absorption is a spectral interference. Detection instruments can correct for some interferences by electronically subtracting the absorption signal from a reference light path that is not open to the atmosphere. However, if two or more gases in the environment absorb the same infrared band, the instrument will measure them as being the same substance and the interference is not easily correctable.

While it would not be very useful to discuss the mathematics associated with light absorbance, noting some basic physical principles will be helpful. First, absorbance of light by a gas sample is dependent on the path length that the light takes through the sample cell. Second, absorbance is also proportional to the concentration of the interacting gas in the instrument's sample cell. Lastly, absorbance is proportional to a property called absorbtivity, which varies with every combination of gas and chosen wavelength. It represents a measure of a material's efficiency in absorbing light.

If the gas one intends to measure has a low absorbtivity, and if the instrument incorporates only a short light path, the gas concentration will have to be high before the instrument detects it. That is, the instrument's detection limit may be inappropriately high and one may not be able to measure low concentrations of gas. The absorbtivity of a gas is an unchangeable property of nature. If one wishes to measure low concentrations of a gas with low absorbtivity, one is forced to design an instrument with a long light path, and possibly use mirrors in the sample cell to accomplish this.

Another fact that can affect instrument performance is related to sample handling. Some infrared instruments are intended for handheld portable use; others are intended for mounting at a fixed location. Many of these instruments use a pump to draw air through the sample cell. Any direct connection between the sample cell and the mine atmosphere would require use of an air filter to prevent dust from soiling or damaging the optical components of the instrument. Frequent cleaning and servicing would otherwise be necessary. An alternative procedure is to carry a container of mine air to a laboratory for off-site analysis. Infrared gas detectors have limited versatility and ruggedness, but they can be used for environmental evaluation in mines with the proper planning and forethought.

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[7] Hydrogen does not absorb in the usual infrared working region, but this is an exception (*14*).

RANGE

The measurement range for an infrared-based gas monitor varies with the specifics of design and usage. The absorption behavior of the specific gas measured, the design of the sample cell, and choices in electrical signal modification determine the response range of the instrument. Instruments are usually designed with one or two given concentration ranges reflecting a particular buyer's measurement interests. They may be built to accurately measure high concentrations or low concentrations, but usually not both. The upper detection limit can be up to 100 pct; the lower detection limit is usually a few hundred parts per million. Lower limits are achievable with careful design that may require specialized, long-path-length sample cells. In general, an instrument can be built for any concentration range of interest. The greatest challenges, however, toward satisfying an instrument user's wishes are at or below the exposure standard level for a particular gas. Infrared instruments have been manufactured that can measure levels of 10 to 20 ppm CO, for alarm use in conjunction with early fire detection.

RESPONSE TIME

Manufacturer literature states that infrared detectors respond very quickly, and any change in gas composition would normally be indicated within 5 to 10 s. Some delay would occur if the gas were sampled from a remote site through tubing. Whatever time the gas spent in transit would have to be added to the instrument response time. If the delay is acceptable, a very long tube could be attached to the detector inlet and an auxiliary pump used to draw the gas.

ACCURACY

As was the case for electrochemical gas monitors, the accuracy of infrared gas monitors depends heavily on how recently the instrument was calibrated. Manufacturers generally report the performance specifications of the product under ideal circumstances. However, even when carefully handled, manufacturers still typically record drifts in readings of 2 pct of full scale in 1 day. Precision for infrared instruments (reproducibility of a reading under set conditions) is typically given as 1 pct of full scale. Instruments should be calibrated before each shift, or as often as experience dictates. Field experience with an instrument can vary with the quality and condition of the product, care in calibration, experience of the operator, and the exact means and circumstances of use. Generally, an instrument should measure the concentration of a gas with a total deviation of no more than several percent. Exact accuracy or precision requirements, however, depend strongly on the objective of the sampling.

Typically available infrared instruments (with one or two small-length sample cells) would not be of sufficient sensitivity to measure SO_2, NO_2, and NO over the concentration ranges of health interest (see table 2), especially at the low end. For example, for SO_2, using a 90-cm-path-length column, the full scale concentration range is 2,000 ppm. With an accuracy of ±1 pct full scale, readings below 20 ppm have an uncertainty of ±20 ppm, which is much greater than the allowed TLV of 2 ppm for SO_2.

INTERFERENTS OR CROSS-SENSITIVITY

By one means or another, every instrument designed to detect a particular gas must attempt to view the wavelength or wavelengths of light absorbed by that gas. Some instruments use a filter that allows only that narrow band of wavelengths to reach the detector (fig. 2). Another option is to use filters to produce a specific wavelength of light that passes through the gas to the detector (fig. 3). Unfortunately, CO and CO_2 absorb light at wavelengths that are quite close to each other on the infrared spectrum (*15*). In fact, an instrument that views a

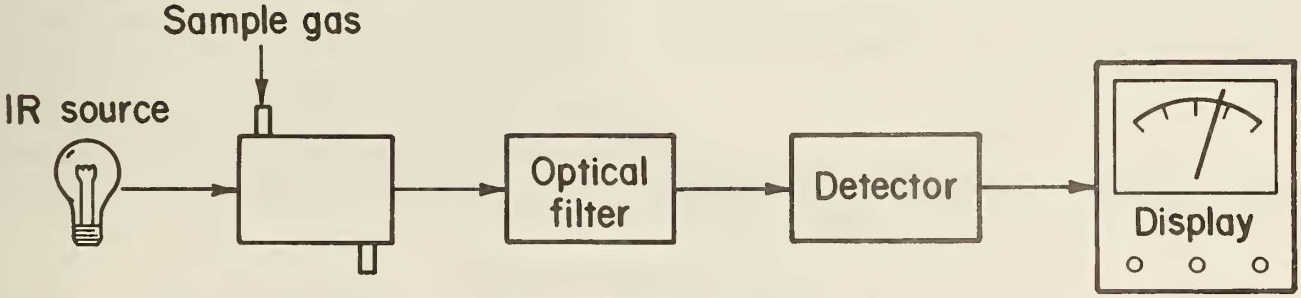

Figure 2.—Infrared sensor with filter immediately before detector.

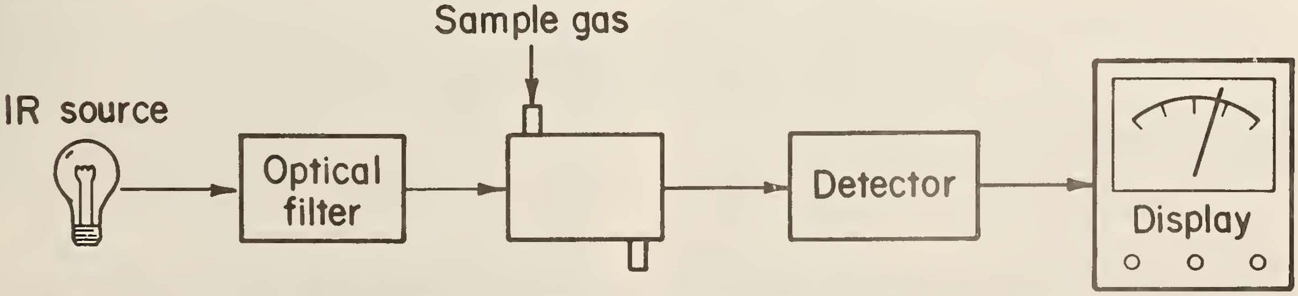

Figure 3.—Infrared sensor with filter immediately after light source.

spectral bandwidth of more than a fraction of 1μm may confuse the two gases. The same situation exists with SO_2 and methane (CH_4) (*15*). Thus, an important factor that will determine whether one gas will interfere with the detection of another is called the instrument's slit width. The slit width is that range of the infrared spectrum that an instrument examines for absorption. The narrower the slit width for an instrument, the more likely only one absorption band from one gas will be measured. The broader the slit width, the more likely that absorption caused by more than one gas will be measured by the instrument. To increase instrument specificity, the slit width should be narrow. On the other hand, to increase signal strength and to avoid background noise in the absorption signal, the slit width should be broad. The design of the instrument must balance the need for specific gas detection with stable absorption signals.

It is general knowledge that some gases, such as water vapor, absorb infrared light in such broad bands that an interference is quite likely if the vapor is present and care is not exercised during instrument choice and design. Many instruments incorporate a reference cell to correct for the undesired absorbance. Using a second wavelength not absorbed by the gas of interest but absorbed by the water vapor only, may provide another means to correct the absorption signal. Special care is sometimes taken in instrument design to see that no part of the light path traverses air outside the sample cell. This prevents ambient water vapor outside the sample cell from causing an interference.

Chemical interferences are also possible for infrared as well as other types of instruments. For this type of problem, the reactivity or instability of the gas examined would be the main cause of concern. For example, oxides of nitrogen (NO, NO_2, and N_2O_4) are in dynamic equilibrium (*16-18*). Depending on temperature, pressure, and especially concentration, the gas molecules may transform into other nitrogen-based substances. These types of reactions tend to be slow at low concentrations (near TLV's), but the general chemistry of nitrogen compounds should be understood before a measurement program is started. Of particular concern are measurements made near the tailpipe of diesel engines. The gases are concentrated and fresh at that point, and prone to change until some stabilizing interaction is reached with the surrounding environment.

POWER

Much of the power required to operate an infrared gas monitor is used to produce infrared light. The present technology used to produce infrared energy requires considerably more power than that required for electrochemical sensors. For instruments that are line operated, power requirements are not a problem. However, if the unit is portable and uses battery power, the batteries will normally have to be recharged at least every shift, but more typically after 4 to 6 h of use. Because of this power requirement, most available infrared instruments are line operated, designed primarily for operation at a fixed measurement location. Infrared instruments are generally not designed to be intrinsically safe, but can be used in nongassy mines or in fresh air locations in gassy mines.

LIFE

The concept of shelf life does not apply to infrared detection instruments. Each component, and the instrument as a whole, may be stored indefinitely without loss of performance. As for operating life, almost all infrared instruments are marketed with a 1-yr warranty; however, these instruments may be expected to operate for much longer periods. Over a number of years, some repairs may be necessary. The device's light source or light detector may fail. Other electrical components may need service after long use. Damage to the instrument from the mine environment is generally of more concern than aging. Deployment in a mine setting may be considered severe use that may not be covered by the manufacturer's warranty. In less rigorous circumstances, infrared instruments are extremely reliable and are more often replaced because of obsolescence rather than malfunction.

COST

The cost of infrared instrumentation is generally much greater than other types of instruments reviewed in this paper. Devices configured for on-site measurement of gases, either for portable, handheld use or for fixed station monitoring, are available for up to $3,000. Custom designs or construction will obviously cost more. For example, sample cells for detection of gases at very low concentration (parts per billion level) may cost several thousand dollars each. Some additional costs will be incurred for calibration equipment and standard gas replacement. Periodic battery replacement costs must be considered for portable, battery-powered units.

GAS DETECTOR TUBES

A gas detector tube is a small, portable device used to provide direct readings of gas concentrations (*19*). Three types of detector tubes are used in mines today: short-term pumped, long-term pumped, and diffusion. All consist of a small glass tube containing a chemically impregnated granular packing (fig. 4). As gas passes through the tube, it reacts with the chemical and produces a color change. The spread of the color change down the length of the tube is related to a given amount of gas drawn or diffusing through the tube. Other gas detector tubes or badges are available that indicate gas concentration by a change in color intensity; however, this type was not considered for diesel exhaust application.

For short-term (several minute) average measurements (grab samples) of a gas concentration at a given site, the tube is broken open at both ends and is fitted into the hand-operated pump or syringe (fig. 5). A certain number of pumps or strokes are performed according to the manufacturer's specifications, drawing a given volume of air through the tube at a given flow rate. An estimation of gas concentration can be read directly by noting where the length of color stain ends on a scale (in parts per million) on the side of the tube.

For work-shift average measurements, a second type of detector tube is used with a battery-powered air pump to draw a gas sample through the tube. An estimation of the average gas concentration over the work shift can be calculated at the end of the shift using the reading of the length of stain on the scale (in microliters) on the side of the tube.

A third type of detector tube uses no pump but depends on gas diffusing into a tube with only one open end. An average gas exposure over the sampling period is obtained by measuring the length of stain with a scale (in parts per million). By dividing this reading by the time of exposure (in hours), the average concentration of gas during the sampling period can be calculated.

RANGE

Stain tubes have been used for many years to measure average gas concentrations. As a result, a wide assortment of tubes are available to measure a number of gases. Table 5 was compiled from specification literature from several manufacturers and lists typical measurement ranges for tubes designed to measure the five gases of interest. The

Table 5.—Typical detection ranges for stain tubes, parts per million

Gas	Short-term	Long-term	Diffusion
CO	5 - 15	2.5- 25	6 - 75
	100 - 700	6.3- 63	
CO_2	100 - 3,000	250 -1,500	1,200 -40,000
	1,000 -12,000		
	5,000 -60,000		
NO[1]	.5- 10	1.3- 12.5	(2)
NO_2	.5- 10	1.3- 13	1.3- 25
SO_2	.5- 5	1.3- 13	.6- 20

[1] This tube actually measures NO_x. To determine NO, one must assume that only NO and NO_2 are present, measure NO_2 separately, and then subtract the value for NO_2 from the value for NO_x.

[2] None available.

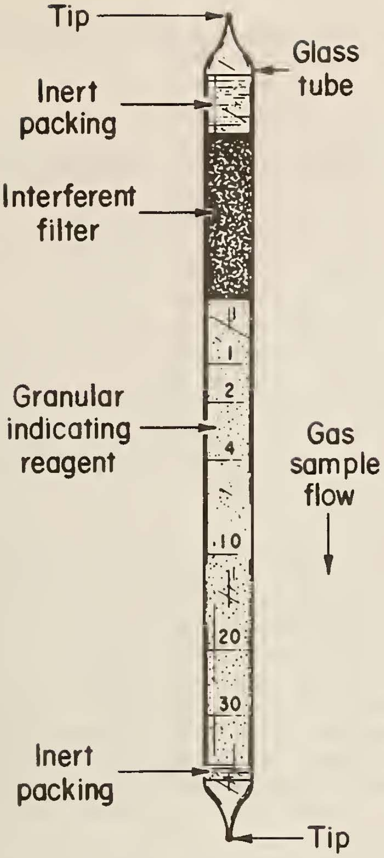

Figure 4.—Gas detector (stain tube).

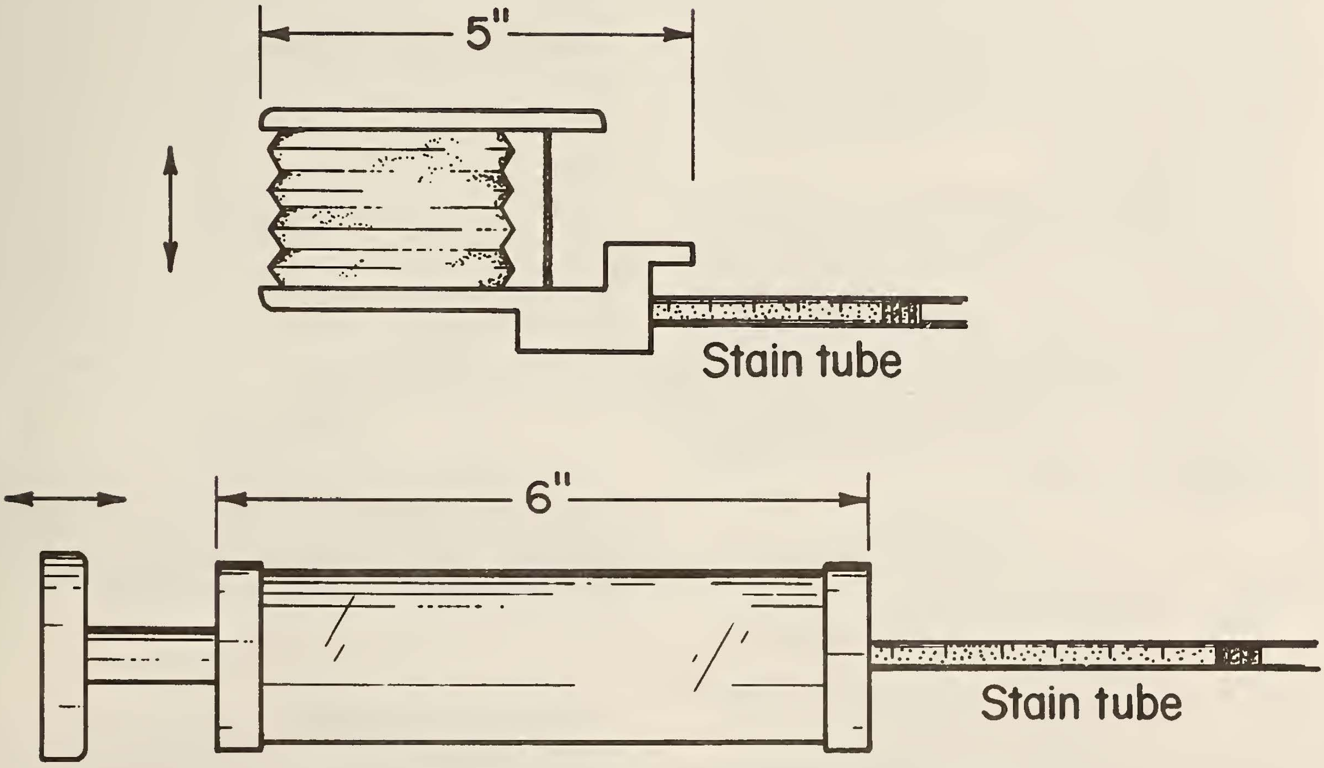

Figure 5.—Hand-operated bellows (top) and syringe (bottom) pump.

table lists separately information about tubes designed for short-term (several minutes), long-term (4-8 h) average measurements, and about diffusion tubes. Once again, prospective buyers are encouraged to check with tube manufacturers because new tubes are occasionally made available as new needs arise.

RESPONSE TIME

Detector tubes are intended for average measurements of gas concentration or exposure. As discussed earlier, short-term tubes that use a hand-operated pump collect samples over several-minute periods. Long-term tubes that use battery-powered pumps collect samples over periods lasting 4 to 8 h. Finally, tubes that depend on diffusion of the gas into the tube usually collect samples over an 8-h work-shift period.

ACCURACY

Unlike electrochemical or infrared instruments, detector tubes are usually not calibrated by the user. If properly manufactured, no calibration is needed. Since conveniently portable sources of stable calibration gases are not available for gases such as SO_2 and NO_2, stain tubes and sampler tubes might be used in preference to electronic instruments that require periodic calibration.

To assure accuracy, however, the tube manufacturer must maintain adequate control during the production process to form reproducible detector tubes. The tube must be evenly packed throughout the entire measuring length with granules of uniform size that are evenly coated with the reactive chemicals. The color change must be of sufficient intensity so that a well-defined interface is formed between the reacted or color-developed tube section and the unreacted section. A well-defined interface is necessary so the stain length can be visually estimated with some certainty. Finally, the manufacturer must be sure of the concentration and purity of the standard gas used to test the tubes during fabrication.

The accuracy of measurements made using tubes that require pumped samples also depends on the care taken by the operator to draw the proper volume of gas through the tube. Hand-operated pumps must be operated the proper number of strokes, and the flow rate of battery-powered pumps must be properly calibrated and periodically checked. The gas sample should be free of water droplets and high concentrations of dust particles. Finally, detector tubes are usually manufactured to read properly at 25° C and at 1 atm barometric pressure. Measurements made at other than these standard conditions must be corrected using the following equation:

$$C = (C_M)(T)/298(P),$$

where C = the corrected reading,
C_M = the reading from the tube,
T = the temperature, K, measured at the sampling site,
and P = the barometric pressure, atm, measured at the sampling site.

Detector tubes previously certified by the National Institute of Safety and Health (NIOSH) are to indicate within ±35 pct of the correct value at concentrations equal to one-half of the TLV, and to within ±25 pct for concentrations within 1, 2, and 5 times the TLV (*19*).

INTERFERENTS OR CROSS-SENSITIVITY

The chemical reaction chosen for the color change should be sufficiently specific so that indications obtained from the tube can be attributed to the gas of interest in a given gas mixture. An experimental assessment of the use of detector tubes for measuring gaseous pollutants from diesel exhaust concluded that the constituents of diesel exhaust include many potent interferents to the measurement of CO, CO_2, NO, NO_2, and SO_2 (*20*). In this work, the detector tubes were found to yield measurements with interference error greater than +35 pct in 40 pct of the CO measurements, and errors greater than –35 pct in 65 pct of the SO_2 measurements.

Many of the chemical reactions used in detector tubes are such that many types of gases will react with a single tube. For example, a tube used to detect CO contains iodine pentoxide, selenium dioxide, and fuming sulfuric acid. In this tube, CO is converted to CO_2, iodine is formed, and a color change from white to brownish green is observed. Other gases that are easily oxidized will also form iodine in this reaction. These gases include acetylene, ethylene, benzene, toluene, trichloroethylene, and hydrogen sulfide. In order to improve the specificity of the CO detector tube, an initial reacting layer is included in some tubes to preoxidize the organic compounds and hydrogen sulfide while passing the CO through. The capacity of the initial reacting layer is limited, of course. If large quantities of interfering gases are present, they may use up the initial reacting layer and pass into the indicating portion of the tube. If large amounts of interfering gases are expected, a tube containing activated charcoal may be placed in front of the CO detecting tube during measurement to remove limited quantities of chloro-organic compounds and many of the higher molecular weight interfering hydrocarbons. Large quantities of water vapor in the air sample can lead to positive errors in the CO determination. At higher concentrations of CO, above 200 ppm, negative errors may occur from direct reaction of the CO with the selenium dioxide in the tube.

The preceding information indicates that in spite of the broad acceptance of the validity of detector tube concentration measurements in industrial hygiene air monitoring, further studies into calibration and interference errors are necessary.

POWER

No electrical power is required to use detector tubes unless a battery-operated pump is used to draw a gas sample through the tube. Note that many pumps available for this application are not intrinsically safe for operation in potentially explosive atmospheres underground.

LIFE

Detector tubes are used for a single measurement and are then discarded. Shelf life is generally listed as 2 yr. Certain tubes, such as some CO detector tubes, require refrigeration (<20° C), and shelf life is usually listed as 1 yr.

COST

Detector tubes cost from \$2 to \$3 each. For a small number of diesel exhaust analyses, stain tubes and sampler tubes may be very useful. For large numbers of analyses, say hundreds per month, electronic instruments such as electrochemical or infrared types may be more cost effective. The initial cost of the hand-operated pump can be as much as \$150. Battery-powered pumps can cost several hundred dollars. Thus, the cost of using detector tubes depends upon the total number of gas samples needed, and must be weighed against the cost of purchasing and maintaining electronic gas detectors over a number of years.

PASSIVE SAMPLER TUBES

Passive sampler or diffusion tubes, called Palmes-type samplers after their inventor (*21*), consist of a tube that is open at one end into which a gas may diffuse (fig. 6). The gas to be analyzed collects on a screen coated with an adsorbent material at the other end of the tube. To collect NO_2 or SO_2, an alkaline adsorbent called triethanolamine is used. Upon adsorbtion, NO_2 is converted into a nitrite ion. After the sampling period is over, the Palmes-type sampler is taken to a separate facility for analysis. The adsorbed nitrite ion is mixed with a chemical reagent to form a deep red color. The concentration of the red color complex and thus the nitrite ion is determined by measuring the adsorbance of light by the solution using a colorimeter. The number of moles of NO_2 collected is then equal to the measured nitrite ion concentration. The average NO_2 concentration is then calculated using the number of moles of NO_2 collected in the equation for Fick's first diffusion law (*21*):

$$C' = [(dm/dt)(L)(R)(T)/(D)(A)(P)] \times 10^{-6} , \qquad (4)$$

where C' = the gas concentration, ppm,
dm = the number of moles of NO_2 collected in the sampler,
dt = the sampling period, s,
L = the tube diffusion length, cm,
R = the gas constant,
T = the temperature,
D = the diffusion coefficient for NO_2 in air, cm^2/s,
A = the tube cross section area, cm^2,
and P = the barometric pressure.

Thus, the concentration of gas in parts per million is proportional to the moles of nitrogen dioxide collected per unit time for a given tube geometry.

RANGE

Palmes-type samplers have successfully been used to measure both NO_x and NO_2 up to 20 ppm (*21*).

RESPONSE TIME

Palmes-type samplers are intended for average measurements of gas concentration or exposure. Samples are usually collected over an 8-h working shift. Unless concentrations of gas are very high, at least 1 h of sampling would be necessary.

ACCURACY

Accuracy has been estimated at ±10 pct at 10 ppm (*21*).

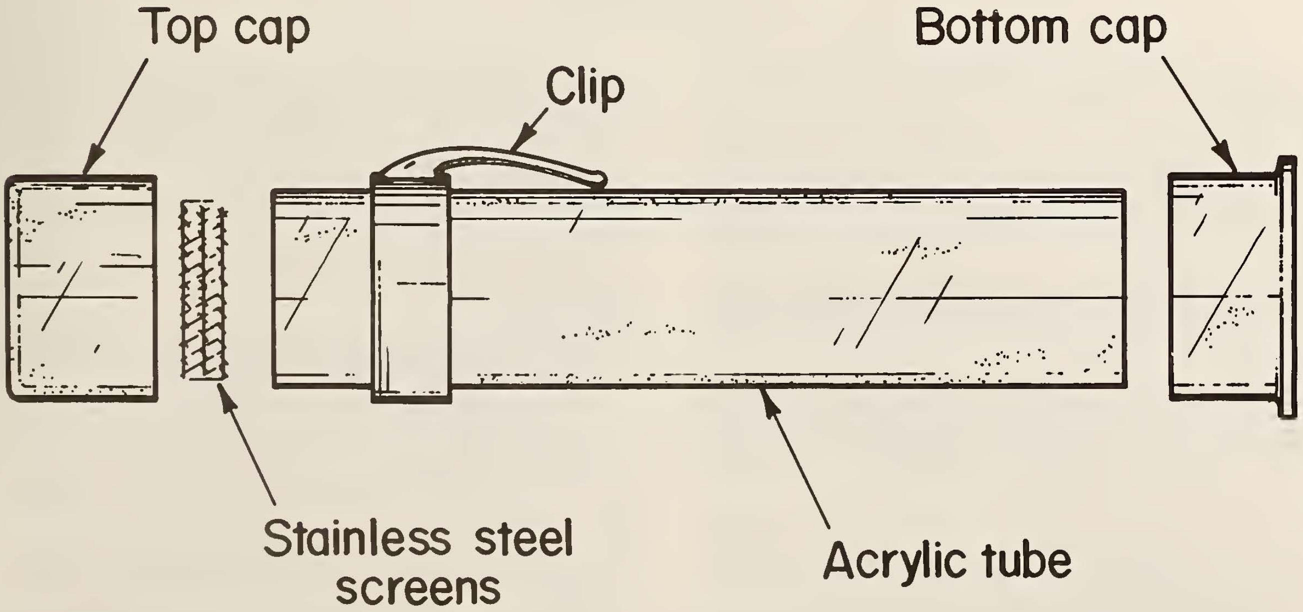

Figure 6.—Passive sampler (Palmes-type).

INTERFERENTS OR CROSS-SENSITIVITY

At this time, no interferents have been identified (*21*).

LIFE

Studies of shelf life have not been conducted; however, tubes should be prepared within several days of scheduled sampling and stored in sealed containers.

COST

Palmes sampler tubes are no longer commercially available; however, they are relatively easy to make (*21*). The body of the sampler can be made simply by cutting lengths of acrylic tubing. The small, round stainless steel screens (fig. 6) can be cut from sheets of stainless steel screen material using a large hole punch. Other assorted parts such as plastic caps and metallic clips can be purchased from supply houses. Complete samplers can be made for less than $1 per unit. Additional cost would be incurred for the colorimetric analyses.

SUMMARY

Intrinsically safe, mine-worthy electrochemical instruments for detecting CO, CO_2, NO, NO_2, and SO_2 have been developed and one or more commercial instruments using electrochemical cells exists for each gas. For CO, electrochemical sensor-based instruments are leading contenders for fulfilling several of the monitoring objectives mentioned at the start of this paper. Intrinsically safe instruments exist that can measure CO concentrations to an accuracy of 2 pct of full scale or better. NO and NO_2, common pollutants in diesel exhaust and interferents for electrochemical CO sensors, as well as ethylene and hydrogen sulfide are easily removed by chemical filters. On the other hand, H_2 is an interferent to electrochemical CO instruments and is not removed by any known chemical filter. In cases with high interferent concentrations, infrared techniques could be used instead of electrochemical instrumentation for measuring CO. Stable gases are available in small, portable metal cylinders for convenient on-site calibration of the CO, CO_2, and NO instruments. On the other hand, low concentration mixtures of NO_2 and SO_2 (2 to 5 ppm) are generally not available in such cylinders, making field calibration difficult.

Suitable infrared instruments are generally not intrinsically safe but can be used in fresh air locations in gassy mines. Infrared instruments are available for in-mine CO and CO_2 concentration measurement; however, infrared instruments are more costly than electrochemical instruments. Generally, portable infrared instruments cannot measure NO, NO_2, or SO_2 at the low levels required by exposure standards.

Stain tubes and passive sampler tubes, especially for measurement of SO_2 and NO_2 at low parts per million concentrations, may be very useful for characterizing air quality. Stain tubes and passive samplers are the only techniques not requiring extensive use of calibration gases. At costs of $2 to $3 per tube, this technique can also be quite cost effective when only a small number of diesel exhaust analyses are required. On the other hand, for measurement requiring accuracy better than ±25 pct or when large numbers of samples must be taken, electrochemical or infrared instrumentation is preferred.

REFERENCES

1. Lioy, P.J., and M.J.Y. Lioy (ed.). Air Sampling Instruments for Evaluation of Atmospheric Contaminants. ACGIH, 6th ed., 1983, 537 pp.
2. Carlson, D.H., and J.H. Johnson. Monitoring Diesel Pollutants in Underground Mines. Soc. Min. Eng. AIME preprint 74-69, 1979, 47 pp.
3. Ferber, B.I., and A.H. Wieser. Instruments for Detecting Gases in Underground Mines and Tunnels. BuMines IC 8548, 1972, 16 pp.
4. Schnakenberg, G.H., and F.N. Kissell. Ventilation Monitoring Instrumentation. Sec. in Underground Mining Methods Handbook, ed. by W.A. Hustrulid. Soc. Min. Eng. AIME, 1982, pp. 1669-1673.
5. Rocky Mountain Center for Occupational and Environmental Health. Development of a Mine Air Contaminant Measurement Program—Diesels and Explosives (contract J0100004). BuMines OFR 80-84, 1983, 74 pp.; NTIS PB 84-183078.
6. Verdin, A. Gas Analysis Instrumentation. McMillan, Halstead, 1973, pp. 187-230.
7. Nader, J.S., T.F. Lauderdale, and C.S. McCammon. Direct Reading Instruments for Analyzing Airborne Gases and Vapors; Air Sampling Instruments for Evaluation of Atmospheric Contaminants. ACGIH, 6th ed., 1983, pp. V1-V118.
8. LaConti, A., and H. Maget. Electrochemical Detection of CO, H_2, and Hydrocarbons in Inert or Oxygen Atmospheres. J. Electrochem. Soc., v. 118, 1971, p. 506.
9. Blazhennova, A.N., G.I. Krukov, and R.N. Saifi. An Apparatus for Electrochemical Analysis (3-electrode gas sensor). United Kingdom Pat. UK 1,101,101, Jan. 31, 1968.
10. Osborn, H.G., and K.F. Blurton. Electrochemical Detection Cell. U.S. Pat. 3,776, 832, Nov. 10, 1970.
11. American Conference of Industrial Hygienists (Cincinnati, OH). Threshold Limit Values and Biological Exposure Indices for 1986-1987, 1986, 111 pp.
12. National Institute for Occupational Safety and Health. NIOSH Pocket Guide to Chemical Hazards. Publ. 78-210, Sept. 1985, 250 pp.
13. Mine Safety and Health Administration. Petitions for Modification of MSHA Mandatory Safety Standards. Mine Safety and Health Reporter, v. 8, No. 13, 1986, p. 304.
14. Skoog, D.A., and D.M. West. Principles of Instrumental Analysis. Saunders College-Holt, Rinehart & Winston, 2d ed., 1980, pp. 113-167, 209-261.
15. Zeller, M.V. Reference Spectra of Gases. Ch. 8 in Infrared Methods in Air Analysis. Perkin-Elmer Corp. Publ. 993-9236, ca. 1976, pp. 68-93.
16. American Conference of Governmental Industrial Hygienists. Documentation of the Threshold Limit Values. 4th ed., 1980, pp. 301-305.
17. Braker, W., and A.L. Mossman. Matheson Gas Data Book. Matheson Gas Products, 5th ed., 1971, pp. 407-408.
18. Zeller, M.V. Infrared Spectra of Nitrogen Oxides. Ch. 5 in

Infrared Methods in Air Analysis. Perkin-Elmer Corp. Publ. 993-9236, ca. 1976, pp. 31-44.

19. Saltzman, B.E. Direct Reading Colorimetric Indicators in Air Sampling Instrumentation. ACGIH, 6th ed., 1983, pp. T-2—T-29.

20. Carlson, D.H., M.D. Osborne, and J.H. Johnson. The Development and Application to Detector Tubes of a Laboratory Method to Assess Accuracy of Occupational Diesel Pollutant Concentration Measurements. AIHA J., v. 43, No. 4, 1982, pp. 275-285.

21. Palmes, E.D., A.F. Gunnison, J. Dimattio, and C. Tomezyk. Personal Sampler for Nitrogen Dioxide. AIHA J., v. 37, 1976, pp. 570-577.

TYPICAL CHEMICAL REACTIONS IN ELECTROCHEMICAL CELLS

2- or 3-Electrode CO Cell

The reaction at the sensing electrode is

$$CO + H_2O = CO_2 + 2H^+ + 2e^-.$$

The reaction at the counter electrode is

$$½\ O_2 + 2H^+ + 2e^- = H_2O.$$

NO Cell

The reaction at the sensing electrode is

$$NO + H_2O = NO_2 + 2H^+ + 2e^-.$$

The reaction at the counter electrode is

$$½\ O_2 + 2H^+ + 2e^- = H_2O.$$

NO_2 Cell

The reaction at the sensing electrode is

$$NO_2 + 2H^+ + 2e^- = NO + H_2O.$$

The reaction at the counter electrode is

$$H_2O = ½\ O_2 + 2H^+ + 2e^-.$$

SO_2 Cell

The reaction at the sensing electrode is

$$SO_2 + 2H_2O = H_2SO_4 + 2H^+ + 2e^-.$$

The reaction at the counter electrode is

$$½\ O_2 + 2H^+ + 2e^- = H_2O.$$

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