8.10 Carbon Monoxide


Detector Types:
A. Nondispersive infrared (NDIR); see Table 8.9a for IR analyzer designs and applications
B. Mercury vapor
C. Gas chromatography
D. Electrochemical fuel cell
E. Catalytic oxidation
F. Others, from color change badges, dosimeter tubes, and radon canisters to mass spectrometers, are discussed in Section 8.60.

Reference Method:
Infrared

Application:
For ambient air monitoring, electrochemical sensors are used most often; for detecting stack gas concentration, infrared sensors are used most often.

Ranges:
A. From 0 to 1, 0 to 5, 0 to 10, 0 to 20, 0 to 50, and 0 to 100 ppm for ambient and 0 to 200, 0 to 500, 0 to 1000, 0 to 2000, 0 to 5000, and 0 to 10,000 ppm for other applications, including stack gas. (See Table 8.9b for overall range capability.)
B. 0 to 50 ppm
C. 0 to 200 ppm
D. 0–50 to 0–500 ppm or more
E. 0 to 500 ppm

Sensitivity:
Generally 1 ppm; chromatographs can provide 0.1 ppm and mercury vapor analyzers 0.05 ppm

Response Times:
Infrared units are usually adjustable down to a few seconds, while electrochemical sensors require 30 to 60 sec.

Inaccuracy:
For NDIR sensors, ±1% of full scale for up to 1000 ppm and ±2 to 3% of full scale for higher ranges. For infrared stack gas analyzers, 2 to 4% of reading can be expected, while for electrochemical ambient monitors, 1 to 3% of full scale is usual.

Costs:
Pocket-size, battery-operated personal toxic gas monitor—$400 to $700; continuous industrial electrochemical or infrared monitor/alarm/transmitter—$400 to $2000; portable, battery-operated flue gas analyzer—$2000 to $5000; mercury vapor analyzer—$7500; NDIR with recorder included—about $10,000; gas chromatograph (see Section 8.12)—$25,000 and up

Partial List of Suppliers:
Advanced Pollution Instruments—API (www.teledyne-api.com)
AMC (Armstrong Monitoring Corp.) (www.armstrongmonitoring.com)
Ametek/Thermox (www.thermox.com)
Bran & Luebbe (www.branluebbe.com)
CEA Instruments (www.ceainstr.com)
Dasibi Environmental Corp. (www.dasibi.com)
Delphian Corp. (www.delphian.com)
Drager Safety Inc. (www.draeger-usa.com)
Ecotech (www.ecotech.com.au)
E&E Process (www.process-controls.com)
INTRODUCTION

Carbon monoxide (CO) is a toxic gas and, as such, it is monitored in the ambient air for personal safety reasons. The threshold limit value (TLV) adopted by the American Conference of Governmental Industrial Hygienists for CO is 50 ppm. In industrial applications, lower limits are often used for alarm set points. Electrochemical and catalytic sensors are used in personal toxic gas monitors.

Carbon monoxide is also an indicator of incomplete combustion and, therefore, it is measured to optimize boilers and other combustion processes (see Figure 8.3k). For these applications, the most frequently used analyzer is the non-dispersive infrared (NDIR) sensor (Section 8.27).

In the chemical processing industries, when higher sensitivity (0.1 ppm) measurements of carbon monoxide are required, mercury vapor and gas chromatographic analyzers (Section 8.12) are also used. Each of these techniques will be briefly described in the discussion that follows.

CALIBRATION TECHNIQUES

Ambient carbon monoxide analyzers (Table 8.10a) are calibrated with gas mixtures of known concentrations. Such mixtures may be prepared by volumetric dilution of pure carbon monoxide with nitrogen or helium, which are free of carbon monoxide. If the volumes used in dilution are accurately known, the concentration may be calculated.

A known small volume of pure carbon monoxide is placed in an evacuated tank of known volume, and the tank is then filled with the dilutor gas. The pressures of the carbon monoxide volume and the final mixture must be known (or else known to be equal). Smaller samples may be prepared in plastic bags by injecting pure carbon monoxide from a gas syringe into a stream of dilutor gas metered accurately into the bag with a flow device such as a wet test meter.

Because cylinder nitrogen commonly has small amounts of carbon monoxide present in it, it must not be assumed to be pure without verification. Pure helium is reliably free of carbon monoxide. A useful procedure is to zero the detector using helium. After that, one can measure the CO content of the available cylinder nitrogen and can make the required correction. This permits using the less expensive nitrogen for most calibrations.

A reference gas mixture whose carbon monoxide content is not accurately known can also be analyzed gravimetrically or volumetrically by various methods, but these techniques are usually less convenient and often require large amounts of gas.

<table>
<thead>
<tr>
<th>Detection Method</th>
<th>Range, ppm</th>
<th>Sensitivity, ppm</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDIR</td>
<td>0–25, 50, 100</td>
<td>0.5–1</td>
<td>U.S. reference method, accurate, stable, dry gases</td>
<td>Sensitive, water, and CO₂ interferences (correctable), zero gas problems</td>
</tr>
<tr>
<td>Mercury vapor (hot HgO + CO releasing Hg vapor)</td>
<td>0–50</td>
<td>0.05</td>
<td>Sturdy, accurate, dry gases, high sensitivity</td>
<td>Interferences by water and other gases</td>
</tr>
<tr>
<td>Gas chromatography (reduction of CO to CH₄, flame ionization detection)</td>
<td>0–200</td>
<td>0.1</td>
<td>Accurate, high sensitivity, also read CH₄, dry gases</td>
<td>Complex and expensive</td>
</tr>
</tbody>
</table>
**Nondispersive Infrared Analyzers**

NDIR analysis is the reference method for the U.S. National Air Quality Standard for carbon monoxide and is discussed in detail in Section 8.27. It allows continuous analysis, because carbon monoxide absorbs the infrared radiation at a wavelength of 4.6 microns. Because infrared absorption is a nonlinear measurement, it is necessary for the analyzer to accurately linearize its output signal.

A schematic diagram of a typical NDIR analyzer is shown in Figure 8.10b. Infrared radiation from a hot filament is chopped to pass alternately through sample and reference cells, to be absorbed in the detector cell divided by a pressure-sensitive diaphragm. If the sample contains carbon monoxide, it will absorb part of the radiation, causing that half of the detector to exert less pressure on the diaphragm, whose distortion is converted to an electrical signal for rectification and amplification.

Sample airflow is continuous at or sometimes above atmospheric pressure. The cell is commonly 0.5 m long. The measuring range usually extends from a minimum of 0.5 to 1 ppm up to a full-scale range of 25 to 100 ppm. Response times are in the range of less than 1 to 5 min. Although the NDIR response is nonlinear, it is assumed to be linear over the limited calibration range in use. Some instruments correct for nonlinearity in the output amplifier. These analyzers can be operated by nontechnical personnel.

**Interferences**

Carbon dioxide and water vapor in the sample interfere with the measurement. Filter cells filled with these gases, or optical filters when placed in front of the cells, can minimize effects of normal atmospheric levels of these interfering gases. The control of water vapor interference by its removal with desiccants (e.g., silica gel) or by a refrigerator condenser is preferable in many cases, even at the cost of some increase in response time.

**Gas Filter Correlation**

When very accurate low-level measurements are needed, or when background gases that have the potential to interfere with the measurement are present, gas filter correlation (GFC) is used (Figure 8.10c). In these designs the measuring and reference filters are replaced by gas-filled cuvettes. The reference cuvette is filled with CO and the measuring cuvette usually with nitrogen.

In addition to being unaffected by the presence of background gases, both the accuracy and the response time of these instruments are better than those using filters. If DFC is used in combination with single-beam, dual-wavelength technology, it is virtually immune to obstruction of the optics. This in turn prevents drift and thereby reduces the frequency at which recalibration is needed.

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**Figure 8.10b**
NDIR carbon monoxide analyzer.

**Figure 8.10c**
GFC-type carbon monoxide analyzer. (Courtesy of Teledyne Technologies Co.)
Carbon monoxide is oxidized by hot mercuric oxide as follows:

$$\text{CO} + \text{HgO}_\text{(s)} \overset{(210^\circ)}{\rightarrow} \text{CO}_2 + \text{Hg(g)} \quad 8.10(1)$$

The mercury vapor released may be measured photometrically. An analyzer based on this principle (Figure 8.10d) can be operated continuously. It has higher sensitivity than does the NDIR type, but it also suffers from some interference. Detection levels go down to 0.025 ppm, and changes of a tenth of that can be observed. Oxygenated hydrocarbons, olefins, and hydrogen interfere with the measurement, but all are normally at much lower concentrations in air than carbon monoxide. Water also interferes and should be removed by a dryer. This instrument has found particular use in nonurban measurements where carbon monoxide levels are low.

**GAS CHROMATOGRAPH**

Gas chromatographs are discussed in detail in Section 8.12. Figure 8.10e illustrates an automated gas chromatograph that is the heart of a high-precision and specificity system measuring methane and carbon monoxide (Figure 8.10e).

A precolumn prevents carbon dioxide, water, and hydrocarbons other than methane from reaching the molecular sieve separation column. After separation, a catalytic nickel reactor converts carbon monoxide to methane, which is detected by flame ionization. The system permits determination of both methane and carbon monoxide about once every 5 min. The output is linear for both components and can be read from 0.1 to 200 ppm. The instrument is relatively complex and expensive, however, and requires technically trained operators.

**ELECTROCHEMICAL ANALYZER**

A galvanic cell for continuous carbon monoxide analysis is based on the reaction of carbon monoxide with iodine pentoxide:

$$5 \text{CO} + I_2O_3 \overset{(150^\circ)}{\rightarrow} 5 \text{CO}_2 + I_2 \quad 8.10(2)$$
The iodine liberated is absorbed by an electrolyte and reaches the cathode of a galvanic cell where it is reduced. The resulting current is measured by a galvanometer. Interference by mercaptan, hydrogen sulfide, hydrogen, olefins, and acetylene may be minimized by sampling through an absorption tube of mercuric sulfate on silica gel. Water vapor interference can be eliminated by the use of a drying column.

The same reaction is used in a coulometric method with a modified Hersch-type cell. The iodine is passed into the cell, and the current flow is measured by an electrometer. The interference possibilities are the same as those for the galvanic analyzer.

The minimum detectable concentration is 1 ppm with good precision if flow rates and temperature are controlled. Careful column preparation is required, and the response time is relatively slow.

**Portable Monitors**

For purposes of personal protection, battery-operated portable units are available. These units are usually provided with one or two alarm set points and with memory for some thousands of data points, together with their times and dates. Table 8.10f lists the ranges, resolutions, and alarm set points for a number of toxic gases, including carbon monoxide.

These pocket-size, battery-operated, portable electrochemical detectors are usually provided with digital displays and audible alarms. They can be configured for one or more monitoring channels. Figure 8.10g illustrates a unit with four individual channels of detection.

**TABLE 8.10f**

Typical Range, Sensitivity, and Alarm Set Points of Portable Personal Protection Monitors

<table>
<thead>
<tr>
<th>Gas</th>
<th>Range</th>
<th>Resolution</th>
<th>Alarm Set Points (low/high)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>0–30%</td>
<td>0.1%</td>
<td>19.5/23.5%</td>
</tr>
<tr>
<td>CO</td>
<td>0–500 ppm</td>
<td>1 ppm</td>
<td>35/200 ppm</td>
</tr>
<tr>
<td>H₂S</td>
<td>0–100 ppm</td>
<td>1 ppm</td>
<td>10/20 ppm</td>
</tr>
<tr>
<td>SO₂</td>
<td>0–20 ppm</td>
<td>1 ppm</td>
<td>2/10 ppm</td>
</tr>
<tr>
<td>NO</td>
<td>0–250 ppm</td>
<td>1 ppm</td>
<td>25/50 ppm</td>
</tr>
<tr>
<td>NO₂</td>
<td>0–20 ppm</td>
<td>0.1 ppm</td>
<td>1/10 ppm</td>
</tr>
<tr>
<td>NH₃</td>
<td>0–50 ppm</td>
<td>1 ppm</td>
<td>25/50 ppm</td>
</tr>
<tr>
<td>PH₃</td>
<td>0–5 ppm</td>
<td>0.1 ppm</td>
<td>1/2 ppm</td>
</tr>
<tr>
<td>Cl₂</td>
<td>0–10 ppm</td>
<td>0.1 ppm</td>
<td>0.5/5 ppm</td>
</tr>
<tr>
<td>HCN</td>
<td>0–100 ppm</td>
<td>1 ppm</td>
<td>4.7/50 ppm</td>
</tr>
</tbody>
</table>


**CATALYTIC ANALYSIS**

The catalyst Hopcalite will oxidize carbon monoxide to carbon dioxide.¹ The resultant temperature rise may be recorded continuously as a measure of carbon monoxide concentration. The catalyst temperature and residence time must be controlled to avoid interference by hydrocarbons. The method is not suitable for most air monitoring applications because of low sensitivity.

**SPOT SAMPLING OF AMBIENT AIR**

When only intermittent analyses are required, it is convenient to collect samples in the field for later analysis in the laboratory. Rigid glass bulbs or stainless steel tanks may be evacuated and then simply opened briefly to collect the air sample. Plastic bags may be filled by means of a small air pump.

The samples may be analyzed later by various means, including use of a continuous analyzer at some other location. The samples may be analyzed in a central laboratory by an infrared spectrophotometer with a long-path gas cell or by suitable gas chromatographic apparatus.
Some colorimetric methods are also available for carbon monoxide analysis, although in general, their sensitivity and precision are low for atmospheric work. An NBS colorimetric indicating gel, if freshly prepared, will limit errors to 5 to 10%, with detectability down to 0.1 ppm. The technique is simple but time-consuming and tedious, with interference by oxidizing and reducing gases.

CONCLUSIONS

As discussed in more detail in Section 8.59, for simple and less accurate measurements of short-term carbon monoxide levels, gel tubes can be used. For continuous and higher precision measurements, nondispersive infrared analysis is the most common.

If it is necessary to also measure methane, the combination gas chromatograph with carbon monoxide analyzer is worthy of consideration, but this is an expensive choice. The mercury vapor analyzer is suitable where the carbon monoxide levels are low.

References


Bibliography