Method for the Continuous Determination of Carbon Monoxide in the Atmosphere by Non-dispersive Infrared Spectrometry

1. FIELD OF APPLICATION

1.1 This method is applicable to the determination of carbon monoxide in ambient air and to the analysis of gases under pressure.

1.2 Range and sensitivity

Instruments are commercially available that measure in the range of 0 to 58 mg/m³, which includes the concentrations most commonly encountered in ambient urban air.

1.3 Interferences

Interferences vary according to the nature of the sample. The interference caused by carbon dioxide is minimal at normal atmospheric concentrations. On the other hand, water vapor can produce an interference equivalent to 12 milligrams of carbon monoxide per cubic metre, if this is not corrected. Water vapor interference can be minimized by (a) passing the air sample through silica gel or similar drying agents, (b) maintaining constant humidity in the sample and calibration gases by refrigeration, (c) saturating the air sample and calibration gases to maintain constant humidity or (d) using narrowband optical filters in combination with some of these measures. Hydrocarbons at the levels found in ambient air do not ordinarily interfere.

1.4 A statement from the manufacturer should be obtained as to the specifications for discrimination against expected interfering substances.

2. PRINCIPLE

This method is based on the absorption of infrared radiation by carbon monoxide. Energy, from a source emitting radiation in the infrared region, is split into two parallel beams, one passing through the sample compartment. The two beams finally pass the detector which consists of two matched cells each containing carbon monoxide. These two cells are separated by a diaphragm. The carbon monoxide in the detector cells only absorbs radiation corresponding to its characteristic frequencies. With a
non-absorbing gas in the reference cell and with no carbon monoxide in the sample cell, the signals from both detectors are balanced electronically. Any carbon monoxide introduced into the sample cell will absorb radiation, which reduces the temperature and pressure in the detector cell and displaces a diaphragm. This displacement is detected electronically and amplified to provide an output signal (10.1).

3. DEFINITIONS

Range – The minimum and maximum measurement limits.

Output – Electrical signal which is proportional to the measurement. Usually expressed as millivolts or milliamps full scale at a given impedance.

Full scale – The maximum measuring limit for a given range.

Minimum detectable sensitivity – The smallest amount of input concentration that can be detected.

Lag Time – The time interval from a step change in input concentration at the instrument inlet to the first corresponding change in instrument output.

Time to 90% response – The time interval from a step change in the input concentration at the instrument inlet to a reading of 90% of the ultimate recorded concentration.

Rise time – The interval between 10% response time and time to 90% response after a step increase in the inlet concentration.

Fall time – The interval between 90% response time and time to 10% response after a step increase in the inlet concentration.

Zero drift – The change in instrument output over a stated time period, usually 24 hours, of unadjusted continuous operation, when the input concentration is zero; usually expressed as percent full scale.

Span drift – The change in instrument output over a stated time period, usually 24 hours, of unadjusted continuous operation, when the input concentration is a stated upscale value; usually expressed as percent full scale.

Operational period – The period of time over which the instrument can be expected to operate unattended within specifications.

Noise – Deviations from the mean output not caused by input concentration changes.
Accuracy — The degree of agreement between a measured value and the true value; usually expressed as ± percent of full scale.

Precision — The degree of agreement between repeated measurements of the same concentration, expressed as the average deviation of the single results from the mean.

Interference — An undesired positive or negative output caused by a substance other than the one being measured.

Interference equivalent — The portion of indicated input concentration due to the presence of an interfering substance or signal.

Operating temperature range — The range of ambient temperatures over which the instrument will meet all performance specifications.

Operating humidity range — The range of ambient relative humidity over which the instrument will meet all performance specifications.

Overload recovery time — The time required for the instrumental system to recover from an overload signal equal to the maximum input of the system.

Linearity — The maximum deviation between an actual instrument reading and the reading predicted by a straight line drawn between upper and lower calibration points.

4. SUGGESTED PERFORMANCE SPECIFICATIONS

Minimum range: 0-58mg/m³.
Minimum output: 0-10, 0-100, 0-1,000 or 0-5,000mV full scale.
Minimum detectable sensitivity: 0.6mg/m³.
Lag time: 15 seconds, maximum.
Time to 90% response: 30 seconds, maximum.
Rise time, 90%: 15 seconds, maximum.
Fall time, 90%: 15 seconds, maximum.
Maximum zero drift: 3% per week — less than 1% in 24 hours.
Maximum span drift: 3% per week — less than 1% in 24 hours.
Precision: Not more than ±0.5%.
Minimum operational period: 3 days.
Noise: Not more than ±0.5%.
Maximum interference equivalent: 1% of full scale.
Minimum operating temperature range: 5-40°C.
Minimum operating humidity range: 10-100%.
Warm-up time: Not more than 1 hour.
Overload recovery time: 30 seconds.
Deviation from linearity: Not more than 1% of full scale.

5. REAGENTS

5.1 Zero gas
Nitrogen or helium in pressure cylinders provided with two-stage regulator valves is required. These gases should contain less than 0.1 milligram carbon monoxide per cubic metre.

5.2 Calibration gases
Calibration gases corresponding to 10, 20, 40 and 80% of full scale are used. These should be provided in pressure cylinders equipped with two-stage regulator valves. Zero and calibration gases should be supplied with certification or guaranteed analysis of carbon monoxide content. Regardless of whether guaranteed analyses are provided or obtained, the user, in his own interest, must check that the degree of linearity of the four standards is sufficient. If this degree of linearity is not obtained during calibration some or all of the calibration gases should be returned to the supplier for correction.

6. APPARATUS

6.1 Carbon monoxide analyzer
Commercially available instruments should be installed on location and demonstrated, preferably by the manufacturer, to meet or exceed manufacturer's specifications and those described in this method. A typical analyzer system is illustrated in Figure 1 (Page 212).

6.2 Sample introduction system
Pump, flow control valve and flowmeter.

6.3 Filter
A filter with a porosity of 2 to 10 microns should be used to prevent large particles from entering the sample cell.

6.4 Moisture control
Refrigeration units are provided with some commercial instruments for maintaining constant humidity. Drying tubes containing indicating
anhydrous calcium sulphate or indicating silica gel may be used. These
should be of large capacity, such as 72 hours or more, so that too frequent
changing may be avoided. These filters must be changed before strike
trough of water. In addition, suitable filters must be installed downstream
from the drying cartridge to prevent the entry, to the optical cells, of
particulate dust from the drying material.

7. OPERATING PROCEDURE

7.1 Specific operating procedures must be supplied by manufacturer in a
detailed manual which corresponds in every detail with the instrument
under test.

7.2 The first step common to all analyzers is to turn on the power supply
and allow the necessary warm-up time before actual operation is begun
using standard or sample gases. This time varies among analyzers and the
length of time the analyzer has spent without power applied. It should not
be more than 30 minutes. In any case, warm-up time should be long enough
to stabilize drift.

7.3 Several classifications of procedures are actually involved. First is
preliminary or initial setup; second, routine operation; and third, trouble
shooting. The first and third classifications should be carried out by a
competent technician. They involve use of internal adjustments, and often
require special electronic instrumentation. Routine operations involve the
use of external controls only and require relatively little training.

7.4 Typical initial or start-up procedures are setting of electrical zero,
making coarse adjustments of infrared sources, oscillator tuning, if used,
signal phase adjusting, amplifier gain adjusting, and initial span and zero
adjusting.

7.5 Routine operations that might ordinarily be involved are described in
the sequence below:

7.5.1 Turn power on.

7.5.2 Allow analyzer to warm up for time period earlier found to be
necessary.

7.5.3 Introduce “zero” gas and adjust zero control to proper reading.

7.5.4 Introduce “span” gases and adjust span control to proper reading.

7.5.5 Check sample flow rate. This must not be in excess of rate found to
cause pressure effects. Minimum rate is adjusted on the requirement for the
resolution of fine sample structure.
7.5.6 Log all operations, control settings, adjustments, and the time of these operations.

7.6 Trouble shooting and maintenance must be carried out routinely and may be required without notice. The principal routine servicing includes replacement of particle filter, water removal check and recorder servicing. Other servicing that can be expected includes sensitivity checks, analyzer signal output determination, infrared source check, amplifier servicing, sample cell cleaning, phase adjustments, and servicing or changing detector. Recorder service requirements are the same as for any similar null-balancing instrument used for signal recording.

8. CALIBRATION

8.1 Calibration curve
Determine the linearity of the detector response at the operating flow rate and temperature. Prepare a calibration curve and check against the curve furnished with the instrument. Introduce zero gas and set the zero control to indicate a recorder reading of zero. Introduce span gas and adjust the span control to indicate the proper value. On the scale of 0 to 58mg/m\(^3\), set the 46mg/m\(^3\) standard at 80\% of full scale on the recorder chart. Recheck zero and span until adjustments are no longer necessary. Introduce intermediate calibration gases and plot the values obtained. If a straight line is not obtained, or if deviation from linearity is not acceptable, the accuracy of the calibration gases should be questioned and some or all of these calibration gases should be returned to the supplier.

9. EXPRESSION OF RESULTS

9.1 Calculations
Determine the concentrations directly from the calibration curve. No calculations are necessary. Carbon monoxide concentrations in mg/m\(^3\) are converted to ppm as follows:

\[ \text{ppm CO} = \text{mg CO/m}^3 \times 0.873 \text{ at } 25^\circ\text{C and 760mm mercury} \]

9.2 Precision and accuracy
Precision determined with calibration gases is ±0.5% full scale in the 0-58mg/m\(^3\) range. Precision is not dependent upon accuracy and precision can be obtained without the values being accurate. Perfect linearity of the calibration curve, for example, may only indicate precision.
A large scale collaborative study of such carbon monoxide measurements has been made (10.2). Carbon monoxide was determined in both dry and humidified air. Using the terminology of Mandel, values for “repeatability” or intralaboratory precision and “reproducibility” or interlaboratory precision, have been established (10.3). For concentrations of carbon monoxide in air up to 60 milligrams per cubic metre, these values are illustrated graphically in Figure 2, taken from the study above cited (Page 212).

From this figure, it is evident that repetition or replication of analyses will not materially assist in increasing the precision of the measurements. It will, in fact, generally be a waste of time and effort. Reproducibility is seen to be optimal at a concentration of 20 milligrams per cubic metre.

The limits of accuracy of such measurements are also given in this study, to which reference should be made. In general terms, the accuracy of the measured carbon monoxide value depends upon both the overall instrumental accuracy and the accuracy with which the known concentrations of carbon monoxide have been made up in the calibration gases. An accuracy of ± 1% of full scale recorder chart can be obtained in the range of 0-58mg/m³ of carbon monoxide. Variations in the temperature, ambient to the analyzer, can cause changes equivalent to as much as 0.5mg CO/m³ per °C. This effect can be minimized by operating the analyzer in a temperature-controlled room. Pressure changes between span checks will cause momentary changes in instrument response. Zero drift is usually less than ±1% of full scale per 24 hours, if cell temperature and pressure are maintained constant.

10. REFERENCES


Fig. 1
Carbon Monoxide Analyzer

Fig. 2
Reproducibility
Repeatability
Concentration CO mg/m³