

Determination of Carbon Monoxide in the Atmosphere using Flame Ionization Detection

1. PRINCIPLE

By employing the correct adsorbants, an air sample may be freed of all components which can give a response in a flame ionization detector, except methane. Carbon monoxide must pass unaltered through the adsorbant. Carbon monoxide and methane are then easily separated chromatographically and carbon monoxide can be conveniently reduced catalytically to methane and measured with a flame ionization detector. The method is semi-continuous, with analysis rate selectable from 4 to 15 samples per hour. Between analyses, the sample stripper column is backflushed.

The instrument should have two modes of operation. One mode should provide for a complete visual display of electrometer output on a meter or strip chart recorder. The second mode should incorporate an automatic zeroing system which switches off when a predetermined change in electrometer output is anticipated, and remains off until the event of interest has passed.

2. APPLICABILITY

The method is applicable to the determination of carbon monoxide in ambient air and to the analysis of gases under pressure. Instruments are commercially available that measure in ranges selectable to a maximum of 6-300ppm ($7-344\text{mg/m}^3$) which includes the concentrations most commonly encountered in ambient urban air and the concentrations likely to be found in localized areas and potentially detrimental to health. The extreme sensitivity of the flame ionization detector is essential for accurate measurement of low levels of carbon monoxide (10.1). Instruments are available which have a 0.02-1ppm range (10.2). Changes in temperature and pressure which could alter the density of the sample must be compensated for by recalibration. Interferences may be examined by directing a stripped, chromatographed sample directly into the flame, by-passing the catalytic converter. Instruments should be equipped to do this. The manufacturer should provide some data on interferences. Conversion of carbon monoxide to methane should be quantitative to achieve maximum sensitivity and reliability.

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, significantly greater than zero, 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 decrease 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 in percent.

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 in percent.

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

Noise – Spontaneous 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 \pm percent of the true value after the effects of interfering substances have been eliminated (physically or mathematically).

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

Specificity – Degree to which the mean measurement is due only to the substance being determined.

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 10 times 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 calibration points.

4. SUGGESTED PERFORMANCE SPECIFICATIONS

Minimum range: 0.02-1 ppm (0.023-1.15mg/m³).

Maximum range: 6-300ppm (7-344mg/m³).

Output (selectable): 0-10, 0-100, 0-1,000 or 0-5,000mV full scale.

Minimum detectable (sensitivity): 0.02ppm (0.023mg/m³).

Lag time: 4 minutes, maximum.

Time to 90% response: 4 minutes, maximum.

Rise time: 2 seconds, maximum.

Fall time: 2 seconds, maximum.

Maximum zero drift: Automatic zeroing.

Maximum span drift: 3% per week – less than 1% in 24 hours.

Precision: Not more than ±0.5%.

Minimum operational period: 3 days.

Specificity: Manufacturer's statement of substances in ambient air other than carbon monoxide which can induce instrument response and the degree of response for each.

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.

Safety features: Automatic fuel shut-off and flame-out indicator.

5. REAGENTS

5.1 *Zero gas*

A sample of CO-free air or air having a low (<0.1ppm) but accurately known CO concentration. This gas is not necessarily for zeroing as calibration is done with automatic zero on. However, suspected interfering gases may be diluted with this zero gas and tested with the instrument.

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. If possible, these gases should be purchased from at least two different suppliers.

5.3 *Flame air*

Compressed air in cylinders, dry and clean enough that any response of the flame ionization detector to contaminants in this air can easily be eliminated electronically. Air containing less than 2ppm hydrocarbon expressed as methane is suitable.

5.4 *Hydrogen*

Compressed hydrogen in cylinders, with a toggle valve in-line for emergency shut-off. The hydrogen should contain less than 0.1ppm hydrocarbon expressed as methane.

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.

6.2 *Sample introduction system*

A vacuum pump to pull the sample through the instrument.

6.3 Filter

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

6.4 Moisture control

When sampling ambient air, care should be taken to ensure that moisture does not enter the tube leading from sampling site to burner manifold. An inverted funnel on the sampling site end of this tube has proved useful in keeping rainwater from entering the tube.

7. OPERATING PROCEDURE

7.1 Specific operating procedures must be supplied by the 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 leak testing gas connections, setting cylinder and instruction gas pressure regulators, flame ignition, zero and span adjusting and connecting the sample pump and inlet tube.

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

7.5.1 Verify the stability of the oven temperature.

7.5.2 Verify calibration with span gases.

7.5.3 Look for signs of column deterioration by examining retention times.

7.5.4 Check for abnormalities in the chromatograms, i.e. negative excursions, excessive noise, etc.

7.5.5 Check sample flow rate. This must not be in excess of rate found to cause pressure effects.

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, replacement of compressed gases and recorder servicing. Other servicing that can be expected includes reactivating chromatography and stripper columns. Recorder service requirements are the same 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 7 to 344mg/m³ set the 275 mg/m³ 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 ppm are converted to mg/m³ as follows:

$$\text{mg CO/m}^3 = 1.145 \cdot \text{ppm CO}$$

at 25° and 760mm mercury.

9.2 *Precision and accuracy*

Precision determined with calibration gases is ±0.5% full scale in the 7-344mg/m³ 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 linearity of detector response, not accuracy. 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 $\pm 1\%$ can be obtained in the range of 0.58mg/m^3 of carbon monoxide.

10. REFERENCES

- 10.1 Stevens, R. K. and O'Keefe, A. E. Modern Aspects of Air Pollution Monitoring. *Analytical Chemistry* **42**, 143A 1970.
- 10.2 Air Sampling Instruments: For Evaluation of Atmospheric Contaminants. 4th Edition 1972. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio.