



# Standard Test Method for Carbon Monoxide in the Atmosphere (Continuous Measurement by Nondispersive Infrared Spectrometry)<sup>1</sup>

This standard is issued under the fixed designation D 3162; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This standard has been approved for use by agencies of the Department of Defense.*

<sup>ε1</sup> NOTE—Editorial corrections were made throughout in September 2000.

## 1. Scope

1.1 This test method is applicable to the determination of the carbon monoxide (CO) concentration of the atmosphere between 0.6 mg/m<sup>3</sup> (0.5 ppm(v)) and 115 mg/m<sup>3</sup> (100 ppm(v)). The measuring principle is based on the absorption of infrared radiation by CO in the 4.7  $\mu$ m region (1).<sup>2</sup>

1.2 The test method has a limit of detection of about 0.6 mg/m<sup>3</sup> (0.5 ppm(v)) carbon monoxide in air.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* See Section 9 for additional precautions.

## 2. Referenced Documents

### 2.1 ASTM Standards:

- D 1356 Terminology Relating to Sampling and Analysis of Atmospheres<sup>3</sup>
- D 1357 Practice for Planning the Sampling of the Ambient Atmosphere<sup>3</sup>
- D 1914 Practice for Conversion Units and Factors Relating to Sampling and Analysis of Atmospheres<sup>3</sup>
- D 3249 Practice for General Ambient Air Analyzer Procedures<sup>3</sup>
- D 3631 Test Methods for Measuring Surface Atmospheric Pressure<sup>3</sup>
- E 1 Specification for ASTM Thermometers<sup>4</sup>
- E 180 Practice for Determining the Precision of ASTM

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D22 on Sampling and Analysis of Atmospheres, and is the direct responsibility of Subcommittee D 22.03 on Ambient Atmospheres and Source Emissions.

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<sup>2</sup> The boldface numbers in parentheses refer to the list of references at the end of the standard.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.03.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 14.03.

Methods for Analysis and Testing of Industrial Chemicals<sup>5</sup>

## 3. Terminology

### 3.1 Definitions:

3.1.1 For definitions of terms used in this test method, refer to Terminology D 1356 and Practice D 3249.

### 3.2 Definitions of Terms Specific to This Standard:

3.2.1 *fall time*—the time interval between initial response and 90 % of final response after a step decrease in input concentrations.

## 4. Summary of Test Method

4.1 An atmospheric sample is introduced into a sample conditioning system and then into a nondispersive infrared spectrometer (NDIR). The spectrometer measures the absorption by CO at 4.7  $\mu$ m using two parallel infrared beams through a sample and a reference cell and a selective detector. The detector signal is conducted to an amplifier control section, and the analyzer output measured on a meter and recording system (2).

4.1.1 Some instruments use gas filter correlation to compare the IR absorption spectrum between the measured gas and other gases present in the gas being sampled, in a single sample cell. These instruments utilize a concentrated sample of CO as a filter for the IR transmitted through the sample cell to produce a beam that cannot be further attenuated by the CO in the sample, and thus produces the reference beam. The broadband radiation that passes through the sample cell and the CO filter is filtered again by a narrow-band-pass filter that allows only the CO-sensitive portion of the band to pass to the detector. The removal of wavelengths sensitive to other gases reduces interferences.

4.2 The concentration of CO in the sample is determined from a calibration curve prepared using standard calibration gases.

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 15.05.

**5. Significance and Use**

5.1 Determination of carbon monoxide is essential to evaluation of many air pollution complexes. This test method derives significance from providing such determination.

5.2 Carbon monoxide is formed in the process of incomplete combustion of hydrocarbon fuels, and is a constituent of the exhaust of gasoline engines. The Environmental Protection Agency (EPA) has set primary and secondary air quality standards for CO that are designed to protect the public health and welfare (3, 4).

5.3 This test method is suitable for measurements appropriate for the purposes noted in 5.1 and 5.2.

**6. Interferences**

6.1 Degree of interference varies among individual instruments. Consult manufacturer's specifications for the particular analyzer to determine whether interferences render the instrument unsuitable for the proposed use.

6.2 The primary interferent is water vapor. With no correction, the error may be as high as 11 mg CO/m<sup>3</sup> map edit n (10 ppm(v)) (5).

6.2.1 Water vapor interference can be minimized by using one of the following steps:

6.2.1.1 Passing the air sample through silica gel or similar drying agent.

6.2.1.2 Maintaining constant humidity in the sample and calibration gases by refrigeration.

6.2.1.3 Saturating the air sample and calibration gases to maintain constant humidity.

6.2.1.4 Using narrow-band optical filters in combination with some of the above measures.

6.2.1.5 Where sample is dried or humidified a volume correction may be necessary.

6.2.1.6 Gas correlation spectrometers minimize interferences and use a narrow-band-pass filter to ensure measuring only the CO-sensitive IR wavelengths.

6.3 Interference may be caused by carbon dioxide (CO<sub>2</sub>). The effect of CO<sub>2</sub> interference at concentrations normally present in ambient air is minimal; that is, 1350 mg (750 ppm(v)) CO<sub>2</sub>/m<sup>3</sup> may give a response equivalent to 0.6 mg CO/m<sup>3</sup> (0.5 ppm(v)) (5).

6.4 Hydrocarbons at concentrations normally found in the ambient air do not ordinarily interfere; that is, 325 mg methane/m<sup>3</sup> (500 ppm(v)) may give a response equivalent to 0.6 mg CO/m<sup>3</sup> (0.5 ppm(v)) (5).

**7. Apparatus**

7.1 *NDIR Carbon Monoxide in Air Analyzer*, complete with voltage transformer, analyzer section, amplifier/control section, meter, and recording system. Analyzer must meet or exceed performance specifications described in Annex A1.

7.2 *Sample Conditioning System*, consisting of pump, flow control valve, pressure relief valve, flowmeter, filter, and moisture control.

7.3 A typical sampling and analyzer system is described in Fig. 1.

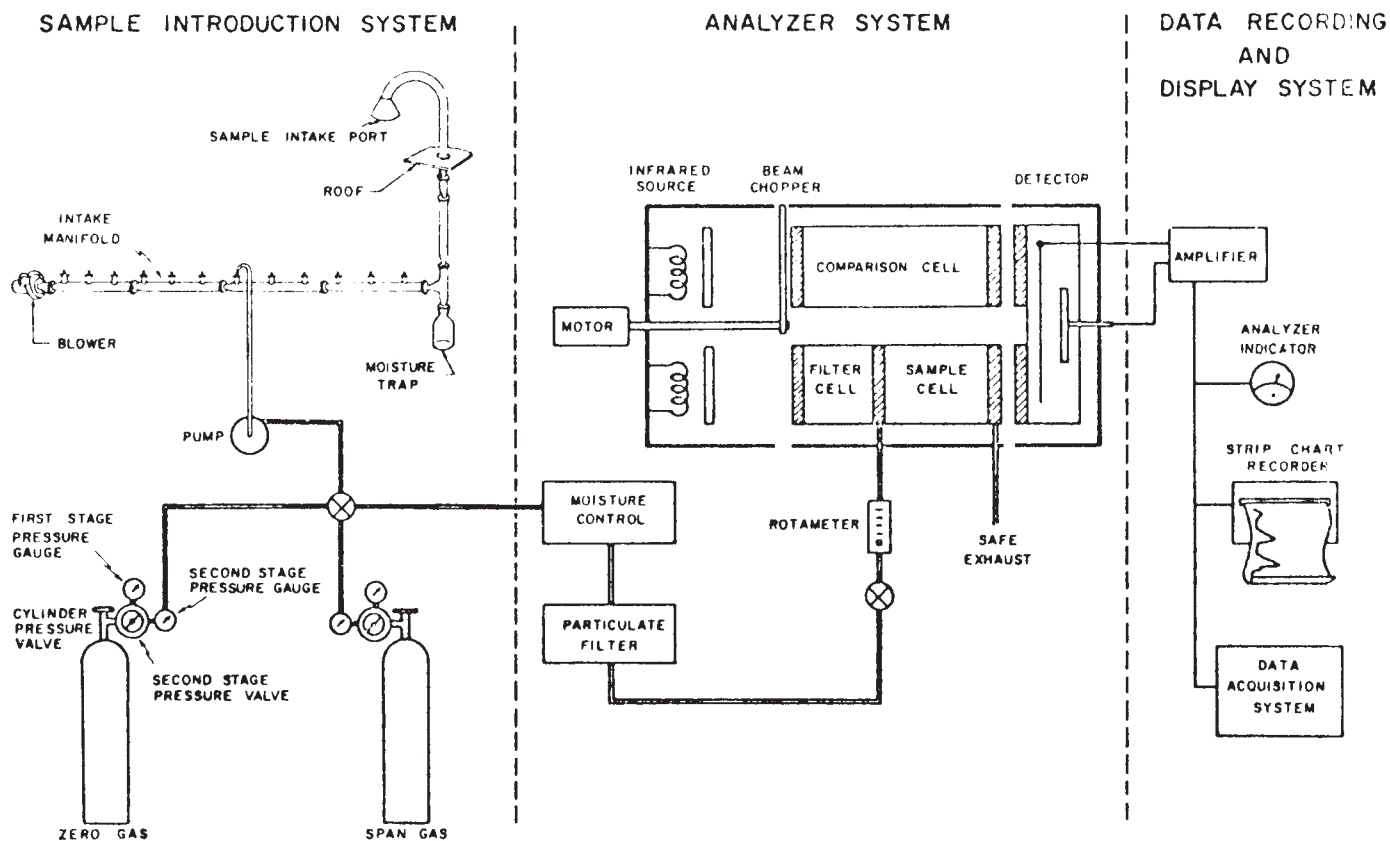


FIG. 1 Carbon Monoxide Monitoring System Flow Chart

7.4 *Thermometer*—ASTM Thermometer 33C meeting the requirements of Specification E 1 will meet the requirements of most applications.

7.5 *Barograph or Barometer*, capable of measuring atmospheric pressure to  $\pm 0.6$  kPa (5 torr). See Test Method D 3631.

## 8. Reagents and Materials

8.1 *Zero Gas*—A pressurized cylinder of pure nitrogen containing less than  $0.1 \text{ mg/m}^3$  CO (0.09 ppm(v)) and having a regulated flow supply.

8.2 *Up-Scale Span Gas*—A pressurized cylinder containing a span gas mixture consisting of CO in air corresponding to 80 % of full scale. A regulated flow system must be provided.

8.3 *Calibration Gases*—Pressured cylinders with regulated flow control are required. These should contain concentrations of CO in air corresponding to the instrument operating range. In order to establish a calibration curve, nitrogen with CO in amounts of 10, 20, 40, and 80 % of full scale are needed.

8.4 *Calibration Certificate*—The span and calibration gases should be certified to be between  $\pm 2$  % of the stated value, and be supplied in high-pressure cylinders with inside surfaces of a chromium-molybdenum alloy of low iron content. Replacement cylinder should be verified by procedures in Annex A3.

## 9. Precautions

9.1 Operate analyzer system in nonexplosive areas unless equipment is explosion-proof.

9.2 The handling and storage of compressed gas cylinders, and the installation and use of the analyzer shall follow Practice D 3249. Cylinders shall not be exposed to direct sunlight.

9.3 Maintain the same sample cell pressure during sampling and calibration. Use the same sample pump.

## 10. Sampling

10.1 *General*—For planning sampling programs, refer to Practices D 1357 and D 3249.

10.2 When sampling the outside ambient atmosphere from an enclosure, a sampling line or probe shall be utilized. It shall extend at least 1 m (3 ft) from the enclosure, and shall be protected against the entry of precipitation.

10.3 Since the analyzer may be temperature-sensitive, it shall be placed in an enclosure with atmosphere control so the temperature remains constant within  $\pm 3^\circ\text{C}$  ( $\pm 5^\circ\text{F}$ ).

10.4 Record the temperature and pressure of the atmosphere sample.

## 11. Calibration and Standardization

11.1 For calibration procedures, refer to Annex A2.

11.2 *Frequency of Calibration:*

11.2.1 *Multipoint Calibration*—A multipoint calibration is required when:

11.2.1.1 The analyzer is first purchased.

11.2.1.2 The analyzer has had maintenance that could affect its response characteristics.

11.2.1.3 When the analyzer shows drift in excess of specifications as determined when the zero and span calibration is performed (see 11.2.2).

11.2.2 *Zero and Span Calibration*—A zero and span calibration is required before and after each sampling period, or, if the analyzer is used continuously, daily.

11.3 *Sample Cell Pressure Gage*—The sample cell pressure gage shall be calibrated in accordance with Annex A2, as follows:

11.3.1 When the analyzer is purchased.

11.3.2 At 6-month intervals.

11.3.3 When the gage shows a change larger than 6.9 kPa (1 psi) during a sampling period in which the flow rate did not change more than  $\pm 0.014 \text{ m}^3/\text{h}$  ( $0.5 \text{ ft}^3/\text{h}$ ).

## 12. Procedure

12.1 After proper calibration has been established, check all analyzer system operating parameters and set the sample flow rate.

12.2 When the analyzer output has stabilized, take the recorder readout and determine the concentration of CO directly from the calibration curve in ppm(v).

12.3 Perform the operational checks described in Annex A4 daily, or during each sampling period (7).

## 13. Calculation

13.1 To convert ppm(v) to  $\text{mg/m}^3$ , refer to Practice D 1914.

## 14. Precision and Bias

NOTE 1—The precision statements are based on an interlaboratory study conducted by Southwest Research Institute, Houston, Tex., in 1972 on 3 samples of carbon monoxide in dry air. Three master cylinders of gas containing nominal concentrations of 8, 30, and  $53 \text{ mg/m}^3$  were prepared and subsamples in high-pressure cylinders were submitted to the collaborating laboratories. Each subsample was analyzed in triplicate and the analyses replicated on 2 more days for a total of 810 determinations. The results from the 15 laboratories were evaluated by the procedure described in Practice E 180.

14.1 *Precision: (6)*

14.1.1 *Triplicate Analysis*—Report the carbon monoxide (CO) content to  $0.1 \text{ mg/m}^3$ . Triplicate runs (Note 2) with a range of  $0.6 \text{ mg/m}^3$  are acceptable for averaging (95 % confidence level).<sup>6</sup>

NOTE 2—Duplicate runs that agree within  $0.5 \text{ mg/m}^3$  are acceptable for averaging (95 % confidence level).

14.1.2 *Repeatability (Single Analyst)*—The standard deviation of the mean (each the average of triplicate determinations) obtained by the same analyst on different days has been estimated to  $0.44 \text{ mg/m}^3$  at 140 df. Two such values should be considered suspect (95 % confidence level) if they differ by more than  $1.2 \text{ mg/m}^3$  (see Note 2).

14.1.3 *Reproducibility (Multilaboratories)*—The standard deviation of the mean (each the average of triplicate determinations) obtained by analysts in different laboratories has been estimated to be  $0.96 \text{ mg/m}^3$  at 11 df. Two such values should be considered suspect (95 % confidence level) if they vary by more than  $3.0 \text{ mg/m}^3$  (see Note 2).

<sup>6</sup> Supporting data giving the results of the collaborative test have been filed at ASTM, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, in Research Report File No. RR: D-22-1000.

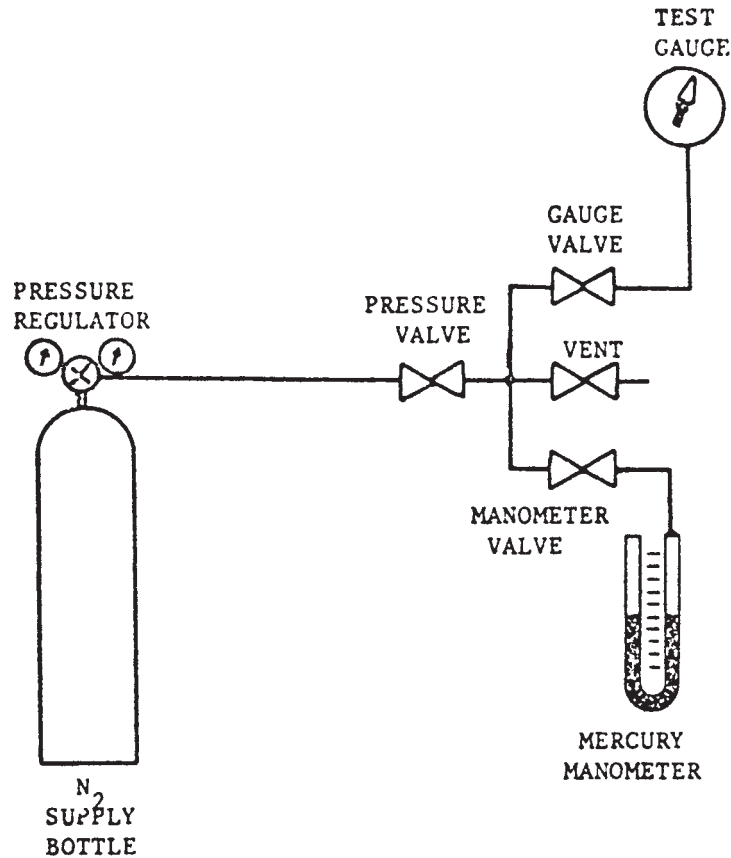


FIG. 2 Calibration Set-up for Pressure Gages

14.2 *Bias*—Since this infrared measurement produces relative values, the bias of the method is dependent on the bias of the calibrations of the gases used in preparing the calibration curve.

**15. Keywords**

15.1 ambient atmospheres; analysis; carbon monoxide; non-dispersive infrared spectroscopy; sampling

**ANNEXES**

**(Mandatory Information)**

**A1. MINIMUM PERFORMANCE SPECIFICATIONS FOR NONDISPERSIVE INFRARED CARBON MONOXIDE ANALYZER**

- A1.1 *Range*—(minimum)—0 to 115 mg/m<sup>3</sup> (0 to 100 ppm(v))
- A1.2 *Limit of Detection*—0.6 mg/m<sup>3</sup> (0.5 ppm(v))
- A1.3 *Rise Time*—(90 %) 5 min (maximum)
- A1.4 *Fall Time*—(90 %) 5 min (maximum)
- A1.5 *Zero Drift*—(±1 %/day and ±2 %/3 days) (maximum)

- A1.6 *Span Drift*—(±1 %/day and ±2 %/3 days) (maximum)
- A1.7 *Precision*—(±4 %) (maximum)
- A1.8 *Operation Period*—(minimum) 3 days
- A1.9 *Noise Level*—±0.5 % of full scale
- A1.10 *Operating Temperature Range*—5 to 40°C
- A1.11 *Operating Temperature Fluctuation*—±5°C
- A1.12 *Linearity*—2 % of full scale

## A2. CALIBRATION PROCEDURES

### A2.1 Analyzer Multipoint Calibration

A2.1.1 *Cylinder Pressure Check*—Check the cylinder pressure of each calibration gas. If a cylinder pressure is less than 2.1 MPa (300 psi), discard the cylinder.

A2.1.2 *Calibration Procedure:*

A2.1.2.1 Turn the analyzer power on, and allow it to sample ambient air for 24 to 48 h to stabilize (or in accordance with manufacturers' instructions).

A2.1.2.2 Connect the zero gas cylinder to the analyzer.

A2.1.2.3 Set pressure of second stage of pressure regulator about 34 kPa (5 psi) above desired sample cell pressure.

**Caution:** Do not exceed pressure limit of sample cell.

A2.1.2.4 Set the sample flow rate to the value to be used during sampling.

A2.1.2.5 Let the zero gas flow until the recorder trace is stabilized or for 5 min, whichever is greater.

A2.1.2.6 Adjust the zero control knob so the trace corresponds to a line representing 5 % of scale.

A2.1.2.7 Repeat A2.1.2.5.

A2.1.2.8 Disconnect the zero gas.

A2.1.2.9 Connect the span gas to the analyzer.

A2.1.2.10 Repeat A2.1.2.3-A2.1.2.5.

A2.1.2.11 Adjust the span control knob until the recorder reads the correct reading, calculated as follows:

$$\left(\frac{C_s}{C_f} \times 100\right) + 5 = S_c \quad (\text{A2.1})$$

where:

$C_s$  = concentration of span gas, ppm(v),

$C_f$  = full-scale reading, ppm(v),

$S_c$  = corrected span reading,

100 = factor to express concentration in percent of range, and

5 = 5 % scale offset.

A2.1.2.12 Let the span gas flow until the trace is stabilized, or for 5 min, whichever is greater.

A2.1.2.13 Disconnect the span gas.

A2.1.2.14 Repeat A2.1.2.2-A2.1.2.8. If no adjustment is requested, proceed to A2.1.2.15. If adjustment of greater than 1 ppm(v) is required, repeat A2.1.2.9-A2.1.2.13.

A2.1.2.15 Lock the zero and span knob controls.

A2.1.2.16 Connect the 10 % span gas cylinder to the analyzer.

A2.1.2.17 Repeat A2.1.2.3-A2.1.2.5. Do not make any adjustments.

A2.1.2.18 Disconnect the cylinder.

A2.1.2.19 Repeat A2.1.2.16-A2.1.2.18 for the 20 and 40 % span gas cylinders.

A2.1.2.20 Prepare a calibration curve of deflection versus percent concentration in ppm(v). Draw a best-fit smooth curve passing through the zero and span points and minimizing the deviation of the intermediate points from the curve. The curve should be either a straight line or bowed in one direction only.

A2.1.2.21 Recheck any calibration point deviating more than  $\pm (1.0 + 0.02 C_c)$  from the smooth curve, where  $C_c$  is the certified concentration of the calibration gas. If the recheck gives the same result, reanalyze the calibration gas.

### A2.2 Zero and Span Calibration Procedures

A2.2.1 Perform procedure in A2.1.

A2.2.2 Perform A2.1.2.9 through A2.1.2.10, using the 80 % span gas. Mark the reading as "unadjusted span." Do not make any adjustments to zero or span.

A2.2.3 Disconnect the span gas cylinder.

A2.2.4 Connect the zero gas cylinder to the analyzer.

A2.2.5 Perform A2.1.2.3-A2.1.2.5. Mark the reading as "unadjusted zero."

A2.2.6 Adjust the zero control knob until the trace corresponds to the true zero setting. Let the zero gas flow until a stable trace is obtained, or for 5 min, whichever is greater. Match the trace as "adjusted zero."

A2.2.7 Disconnect the zero gas cylinder.

A2.2.8 Connect the span gas cylinder to the analyzer.

A2.2.9 Perform A2.1.2.10-A2.1.2.15.

### A2.3 Pressure Gage Calibrations

A2.3.1 *Apparatus*—Mercury manometer cylinder of zero gas, two stage regulator set up as in Fig. 2, and calibrated wall barometer.

A2.3.2 *Procedure:*

A2.3.2.1 Open the cylinder pressure valve.

A2.3.2.2 Adjust the second stage of the regulator until the second-stage pressure gage reads 138 kPa (20 psi).

A2.3.2.3 Open the manometer valve slowly, and allow it to stabilize.

A2.3.2.4 Open the test gage valve slowly, and allow it to stabilize.

A2.3.2.5 Read the pressure indicated by the manometer.

A2.3.2.6 Determine the ambient atmospheric pressure from the wall barometer.

A2.3.2.7 Compute the pressure at the test gage in accordance with Test Method D 3631.

A2.3.2.8 Record  $P_r$  and the actual reading of the gage.

A2.3.2.9 Repeat A2.3.2.2-A2.3.2.8, for 172 kPa (25 psi) and then 207 kPa (30 psi).

A2.3.2.10 Prepare a calibration curve.



### A3. PROCEDURE FOR VALIDATION OF REPLACEMENT SPAN GAS CYLINDER

A3.1 Set up the analyzer, and prepare a calibration curve using old span gases, in accordance with A2.1.

A3.2 Connect the replacement gas cylinder to the analyzer.

A3.3 Perform A2.1.2.3-A2.1.2.5.

A3.4 If the replacement cylinder has a measured value between  $\pm (1.0 + 0.02 C_c)$  ppm(v), where  $C_c$  is the certified value, accept the cylinder. If the value does not agree, have the cylinder recertified.

### A4. OPERATIONAL CHECKS

A4.1 *Zero and Span Knob Setting*—If the required zero and span correction performed in accordance with A2.2 are greater than  $\pm 1.0$  ppm(v), have the analyzer serviced.

A4.2 *Sample Flow Rate*—If the sample flow rate has changed greater than  $\pm 20\%$  from the initial value, check the particulate filter for plugging, and the sample pump for faulty operation. Check the filter monthly by measuring the flow with and without the filter in use. Replace the filter if the indicated flow differential is greater than 5%. Clean or replace the rotameter when it acts sporadically.

A4.3 *Sample Cell Pressure*—If the sample cell pressure increased more than  $\pm 10\%$  of the initial value, have the analyzer serviced.

A4.4 *Temperature Control*—Check the temperature of the shelter or room in which the analyzer is located. If it has

changed greater than  $\pm 3^\circ\text{C}$  ( $\pm 5^\circ\text{F}$ ), have the heating-cooling system serviced.

A4.5 *Water Vapor*—Perform the check specified in the analyzer's instruction manual.

A4.6 *Analog Recording System*—Check the strip chart recorder for the following:

A4.6.1 Chart speed setting.

A4.6.2 Gain control setting.

A4.6.3 Ink supply.

A4.6.4 Paper supply.

A4.6.5 Sign of excess noise.

A4.6.6 Proper operation of analyzer.

A4.6.7 Time mark, sign, and date the record.

A4.7 *Digital Recorder*—Perform the check in accordance with the manufacturer's instructions.

### REFERENCES

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