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Ambient air — Determination of carbon monoxide — Non-dispersive infrared spectrometry method

Air ambiant — Dosage du monoxyde de carbone — Méthode par spectrométrie dans l'infrarouge selon un procédé de type non dispersif

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 4224 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 3, *Ambient air*.

Annexes A, B and C form a normative part of this International Standard.

Introduction

Determination of carbon monoxide (CO) is an essential component of the evaluation of many air pollution complexes. Carbon monoxide is formed in the process of incomplete combustion of hydrocarbon fuels, and is a constituent of the exhaust of gasoline engines. Various national air quality regulatory bodies have established air quality standards for CO that are designed to protect the public health and welfare.

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Ambient air — Determination of carbon monoxide — Non-dispersive infrared spectrometry method

1 Scope

This International Standard specifies a non-dispersive infrared spectrometry method for the continuous analysis and recording of the carbon monoxide (CO) content of the ambient air.

The method is applicable to the determination of carbon monoxide concentrations from 0,6 mg/m³ (0,5 ppm volume fraction) to 115 mg/m³ (100 ppm volume fraction).

The method has a lower limit of detection of about 0,06 mg/m³ (0,05 ppm volume fraction) carbon monoxide in air.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO/TR 4227, *Planning of ambient air quality monitoring*.

ISO 6141, *Gas analysis — Requirements on certificates for gases and gas mixtures*.

ISO 6142, *Gas analysis — Preparation of calibration gas mixtures — Gravimetric method*.

ISO 6143, *Gas analysis — Determination of composition of calibration gas mixtures — Comparison methods*.

ISO 6144, *Gas analysis — Preparation of calibration gas mixtures — Static volumetric method*.

ISO 6146, *Gas analysis — Preparation of calibration gas mixtures — Manometric method*.

ISO 6147, *Gas analysis — Preparation of calibration gas mixtures — Saturation method*.

ISO 6879, *Air quality — Performance characteristics and related concepts for air quality measuring methods*.

ISO 9169, *Air quality — Determination of performance characteristics of measurement methods*.

3 Principle

An atmospheric sample is introduced into a sample conditioning system and then into a non-dispersive infrared spectrometer (NDIR).

The spectrometer measures the absorption by CO at $4,7\text{ }\mu\text{m}$ [1] using two parallel infrared beams through a sample cell, a reference cell and a selective detector. The detector signal is fed to an amplifier control section and the analyser output measured on a meter and recording system.

Some instruments use gas filter correlation to compare the IR absorption spectrum between the measured gas and other gases present in the sample, in a single sample cell. These instruments utilize a highly concentrated sample of CO as a filter for the IR transmitted through the sample cell, to yield a beam that cannot be further attenuated by the CO in the sample and thus acts as a reference beam. The broadband radiation that passes through the sample cell and the CO filter is filtered again by a narrow-bandpass 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.

The concentration of CO in the sample is determined from a calibration curve [2].

4 Interferences

4.1 General

The degree of interference which occurs varies among individual NDIR instruments. Consult the manufacturer's specifications for the particular analyser to determine whether interferences render the instrument unsuitable for the proposed use.

4.2 Water vapour

The primary interferant is water vapour, and is a function of the water vapour content in the sample gas. With no correction, the error may be as high as 11 mg/m^3 (10 ppm volume fraction) [5].

Water vapour interference can be minimized by using one or more of the following procedures:

- a) passing the air sample through a semi-permeable membrane or a similar drying agent;
- b) maintaining a constant humidity in the sample and calibration gases by refrigeration;
- c) saturating the air sample and calibration gases to maintain constant humidity;
- d) using narrow-band optical filters in combination with some of the above measures;
- e) making a volume correction, if the sample is dried or humidified.

NOTE Gas-correlation spectrometers facilitate rejection of interference by water vapour, carbon dioxide and organic compounds, therefore use of a narrow-band-pass filter ensures that only the CO-sensitive IR wavelengths are measured.

4.3 Carbon dioxide

Interference may be caused by carbon dioxide (CO_2). The effect of CO_2 interference at concentrations normally present in ambient air is minimal; that is, 600 mg/m^3 (340 ppm volume fraction) of CO_2 may give a response equivalent to $0,2\text{ mg/m}^3$ (0,2 ppm volume fraction) [3]. If necessary, CO_2 may be scrubbed with soda lime.

4.4 Hydrocarbons

Hydrocarbons at concentrations normally found in the ambient air do not ordinarily interfere; that is, 325 mg/m^3 (500 ppm volume fraction) of methane may give a response equivalent to $0,6\text{ mg/m}^3$ (0,5 ppm volume fraction) [3].

5 Apparatus

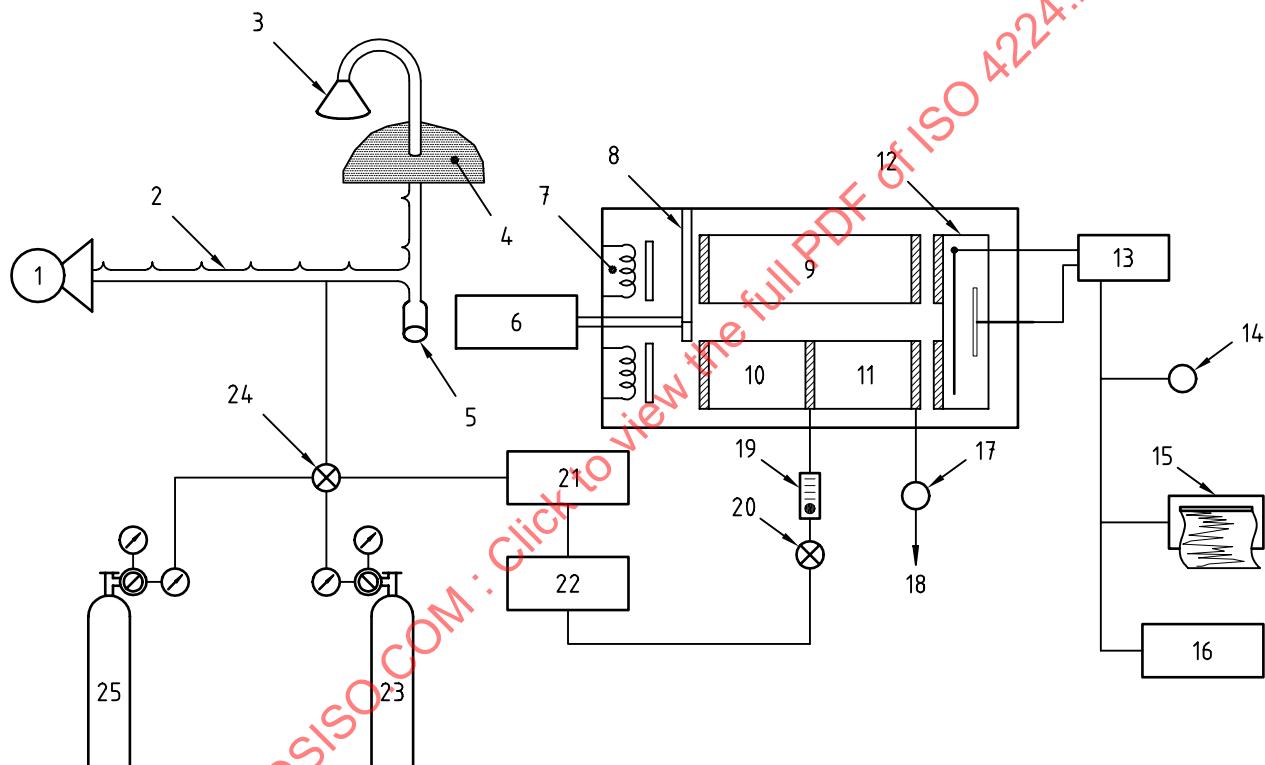
5.1 NDIR analyser, for analysis of carbon monoxide in air.

The analyser should be complete with analyser section, sample pump, amplifier/control section, meter, and recording system. The NDIR analyser shall meet the performance specifications described in annex A. See Figure 1.

5.2 Sample conditioning system, consisting of flow control valve, rotameter, particulate matter filter, and moisture controller.

5.3 Thermometer, capable of measuring atmospheric temperature to $\pm 0,5\text{ }^{\circ}\text{C}$.

5.4 Barograph or barometer, capable of measuring atmospheric pressure to $\pm 0,6\text{ kPa}$.



Key

1	Blower	14	Analyser readout
2	Sample manifold	15	Strip chart recorder
3	Sample inlet port	16	Data acquisition system
4	Roof	17	Pump
5	Moisture trap	18	Exhaust
6	Motor	19	Rotameter
7	Infrared source	20	Flow control valve
8	Beam chopper	21	Moisture controller
9	Reference cell	22	Particulate matter filter
10	Filter cell	23	Span gas
11	Sample cell	24	Four-way valve
12	Infrared detector	25	Zero-air
13	Amplifier		

Figure 1 — Typical carbon monoxide analyser system

5.5 Calibration equipment

The two acceptable methods for dynamic multipoint calibration of CO analysers are:

- a) the use of individual certified standard cylinders of CO for each concentration needed;
- b) the use of one certified standard cylinder of CO, diluted as necessary with zero-air, to obtain the various calibration concentrations needed.

Both methods require the following equipment.

5.5.1 Pressure regulators for the CO cylinders

A two-stage regulator with inlet and delivery pressure gauges will be required for the CO calibration standard cylinder. Procure regulators for each cylinder if individual cylinders are to be used for individual calibration points. Ensure the cylinders have a non reactive diaphragm and suitable delivery pressure. Consult the supplier from whom the CO cylinders are to be obtained for the correct cylinder fitting size required for the regulator.

5.5.2 Flow controller

The flow controller can be any device (valve) capable of adjusting and regulating the flow from the calibration standard: If the dilution method is to be used for calibration, a second device is required for the zero-air. For dilution, the controllers shall be capable of regulating the flow to $\pm 1\%$.

5.5.3 Flow meter

A calibrated flow meter capable of measuring and monitoring the calibration standard flowrate. If the dilution method is used, a second flow meter is required for the zero-air flow. For dilution, the flow meters shall be capable of measuring the flow with an accuracy of $\pm 2\%$.

5.5.4 Mixing chamber (dynamic dilution only)

A mixing chamber is required only if the calibrator concentrations are generated by dynamic dilution of a CO standard. Design the chamber to provide thorough mixing of CO and zero-air.

5.5.5 Output manifold

The output manifold should be of sufficient diameter to ensure an insignificant pressure drop at the analyser connection. The system shall have a vent designed to ensure atmospheric pressure at the manifold and to prevent ambient air from entering the manifold.

6 Regents and materials

6.1 Zero-air

Use a pressurized cylinder of pure air certified to contain less than $0,1\text{ mg/m}^3$ ($0,09\text{ ppm}$ volume fraction) of CO. Alternatively, a catalytic oxidizing agent to convert CO to CO_2 or a palladium filter may be used to obtain zero-air.

6.2 Up-scale span gas

Use a pressurized cylinder containing a span gas mixture consisting of CO in air corresponding to 80 % of full scale. Certify the cylinder in accordance with ISO 6142, ISO 6143, ISO 6144, ISO 6146 or ISO 6147.

6.3 Calibration gases

Use pressurized cylinders containing concentrations of CO in air corresponding to the instrument operating range, that is, 10 %, 20 %, 40 % and 80 % of full-scale range. They shall be certified to a national standard.

Alternatively, if a dilution calibration method is used, a single pressurized cylinder may be used. This may be in nitrogen if the zero-air dilution ratio is not less than 100:1.

Utilize high-pressure cylinders with inside surfaces of a chromium-molybdenum alloy with low iron content for the up-scale and calibration gases.

6.4 Calibration certificate

Certify the span and calibration gases to $\pm 2\%$ of the stated value. See ISO 6141.

7 Precautions

Operate the analyser system in non explosive areas unless the equipment is explosion-proof.

Follow standard safety practices for the handling and storage of compressed gas cylinders and the installation and use of the analyser. See ISO 6142.

Do not expose cylinders of compressed gases to direct sunlight or excessive heat.

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

8 Sampling

When sampling the outside ambient atmosphere from an enclosure, utilize a sampling line or probe extending at least 1 m from the enclosure, and protected against the entry of precipitation. See ISO/TR 4227.

Place the analyser in an enclosure with atmospheric control so the temperature remains constant within $\pm 5\text{ }^{\circ}\text{C}$.

Record the temperature and pressure of the atmosphere sample.

9 Calibration and standardization

9.1 Calibration procedures

Calibration procedures shall be in accordance with annex B.

9.2 Frequency of calibration

9.2.1 Multipoint calibration

Perform a multipoint calibration (see B.1) when:

- the analyser is first purchased;
- the analyser has had maintenance that could affect its response characteristics;
- the analyser shows drift in excess of specifications as determined when the zero and span calibrations are performed (see 9.2.2).

9.2.2 Zero and span calibration

Perform zero and span calibrations (see B.2) before and after each sampling period or, if the analyser is used continuously, daily.

10 Procedure

Determine the performance characteristics in accordance with ISO 9169.

Establish calibration, check the analyser system operating parameters, and set the sample flowrate.

When the analyser output has stabilized, take the recorder readout and determine the concentration of CO directly from the calibration curve in milligrams per cubic metre or in ppm volume fraction, depending on the analyser output. See clause 11 to convert ppm volume fraction to milligrams per cubic metre.

Perform the operational checks required in annex C daily, or during each sampling period [5].

11 Calculation

To convert ppm volume fraction to milligrams per cubic metre, use the following equation :

$$\rho_1 = \frac{\rho_2 \times m_r \times 298 p}{24,45 \times T \times 101,3}$$

where

- ρ_1 is the CO concentration, expressed as milligrams per cubic metre;
- ρ_2 is the CO concentration, expressed as ppm volume fraction;
- m_r is the molar mass of carbon monoxide, (28 g/mol);
- 298 is the standard absolute temperature, in kelvin;
- p is the measured gas pressure, in kilopascals;
- 24,45 is the molecular volume of 1 mole, in litres;
- T is the measured absolute gas temperature, in kelvin;
- 101,3 is the standard gas pressure, in kilopascals.

12 Precision and bias

NOTE The precision statements are based on an interlaboratory study conducted by Southwest Research Institute, Houston, TX, USA, in 1972 on samples of carbon monoxide in dry air. Three master cylinders of gas containing nominal concentrations of 8 mg/m³, 30 mg/m³ and 53 mg/m³ were prepared and subsamples in high-pressure cylinders were submitted to the collaborating laboratories. Each subsample was analysed in triplicate and the analyses replicated on two more days for a total of 810 determinations.

12.1 Precision [4]

12.1.1 Triplicate analysis

Report the carbon monoxide (CO) content to the nearest 0,1 mg/m³. Triplicate runs with a range of 0,6 mg/m³ are acceptable for averaging (95 % confidence level).¹⁾

NOTE Duplicate runs that agree within 0,5 mg/m³ are acceptable for averaging (95 % confidence level).

12.1.2 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 be 0,44 mg/m³ at 140 degrees of freedom. Two such values should be considered suspect (95 % confidence level) if they differ by more than 1,2 mg/m³ (see Note in 12.1.1).

12.1.3 Reproducibility (multilaboratory)

The standard deviation of the mean (each the average of triplicate determinations) obtained by analyst in different laboratories has been estimated to be 0,96 mg/m³ at 11 degrees of freedom. Two such values should be considered suspect (95 % confidence level) if they vary by more than 3,0 mg/m³ (see Note in 12.1.1).

12.2 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.

1) Supporting data giving the results of the collaborative study have been filed at ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428, USA, in Research Report File No. RR:D022-1000.

Annex A (normative)

Minimum performance specifications for non-dispersive infrared carbon monoxide analyser

Range (minimum): 0 to 115 mg/m³ (0 to 100 ppm volume fraction)

Rise time (90 %): 5 min (maximum)

Fall time (90 %): 5 min (maximum)

Zero drift: ± 1 % per day of upper range limit or of applicable range

Span drift: ± 1 % per day and ± 2 % per 3 days (maximum)

Precision: ± 4 % (maximum)

Operation period (minimum): 3 days

Noise level: $\pm 0,5$ % of full scale or linearly decreased to zero scale

Operating temperature range: 5 °C to 40 °C

Operating temperature fluctuation: ± 5 °C

Linearity: 2 % of full scale

Annex B (normative)

Calibration procedures

B.1 Analyser multipoint calibration

B.1.1 Cylinder pressure check

Check the pressure of each calibration gas cylinder. If a cylinder pressure is less than 2 MPa, discard the cylinder.

B.1.2 Calibration procedure

B.1.2.1 Procedure using dynamic dilution method.

- a) Assemble a dynamic calibration system such as that shown in Figure B.1. Introduce the calibration gases, including zero-air, into the sample inlet of the analyser.
- b) Calibrate the flowmeters under the conditions of use against an authoritative standard such as a soap-bubble meter or wet-test meter. Correct the volumetric flowrates to 298 K and 101,3 kPa. Calibrate the flowmeter in accordance with ISO 6158.
- c) Select the operating range of the CO analyser to be calibrated.
- d) Connect the signal output of the CO analyser to the input of the strip chart recorder or other data collection device. Base the adjustments to the analyser on the appropriate strip chart or data device readings. References to analyser responses in the procedure given below refer to recorder or data-device responses.
- e) Adjust the calibration system to deliver zero-air to the output manifold. The total air flow shall exceed the total demand of the analyser connected to the output manifold, to ensure that no ambient air is pulled into the manifold vent. Allow the analyser to sample zero-air until a stable response is obtained. After the response has stabilized, adjust the analyser zero control. Offset the analyser zero adjustments to + 5 % of scale to facilitate observing negative zero drift. Record the stable zero-air response as Z_{CO} .
- f) Adjust the zero-air flow and the CO flow from the standard CO cylinder to provide a diluted CO concentration of approximately 80 % of the upper range limit (URL) of the operating range of the analysers connected to the output manifold, to ensure that no ambient air is pulled into the manifold vent. Calculate the CO concentration:

$$[CO]_{OUT} = \frac{[CO]_{STD} \times q_{CO}}{q_D + q_{CO}}$$

where

$[CO]_{OUT}$ is the diluted CO mass concentration at the output manifold, in milligrams per cubic metre (ppm volume fraction);

$[CO]_{STD}$ is the mass concentration of the undiluted CO standard, in milligrams per cubic metre (ppm volume fraction);

q_{CO} is the flowrate of the CO standard corrected to 298 K and 101,3 kPa, in litres per minute;

q_D is the flowrate of the dilution air corrected to 298 K and 101,3 kPa, in litres per minute. Adjustments to zero span.

g) Sample this CO concentration until a stable response (\pm of nominal upper range limit) is obtained. Adjust the analyser span control to obtain a recorder response as indicated below:

$$\text{Recorder response (percent scale)} = \left(\frac{[\text{CO}]_{\text{OUT}}}{\text{URL}} \times 100 \right) + Z_{\text{CO}}$$

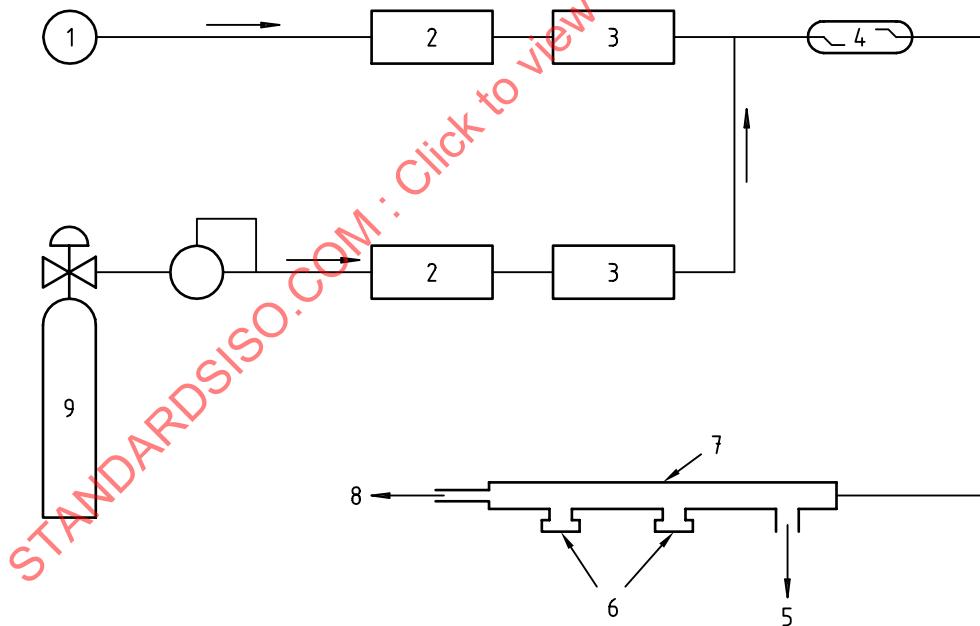
where

URL is the nominal upper range limit of the analyser's operating range, and

Z_{CO} is the analyser response to zero-air, as percent scale.

h) If substantial adjustment to the analyser span control is required, it may be necessary to recheck the zero and span adjustments by repeating steps e) and f). Record the CO mass concentration and the analyser response.

i) Generate several additional concentrations (at least three evenly spaced points across the remaining scale are suggested to verify linearity) by decreasing q_{CO} or increasing q_D . Recheck any calibration point deviating more than $\pm(1,0 + 0,02 [\text{CO}]_{\text{STD}})$ from the smooth curve. If the recheck gives the same result, reanalyse the calibration gas. Ensure that the total flow exceeds the analyser total flow demand. For each concentration generated, calculate the exact CO mass concentration using the equation in step f). Record the concentration and the analyser response for each concentration. Draw a best-fit regression curve passing through the zero and span points, in accordance with ISO 9169. The curve shall be linear.



Key

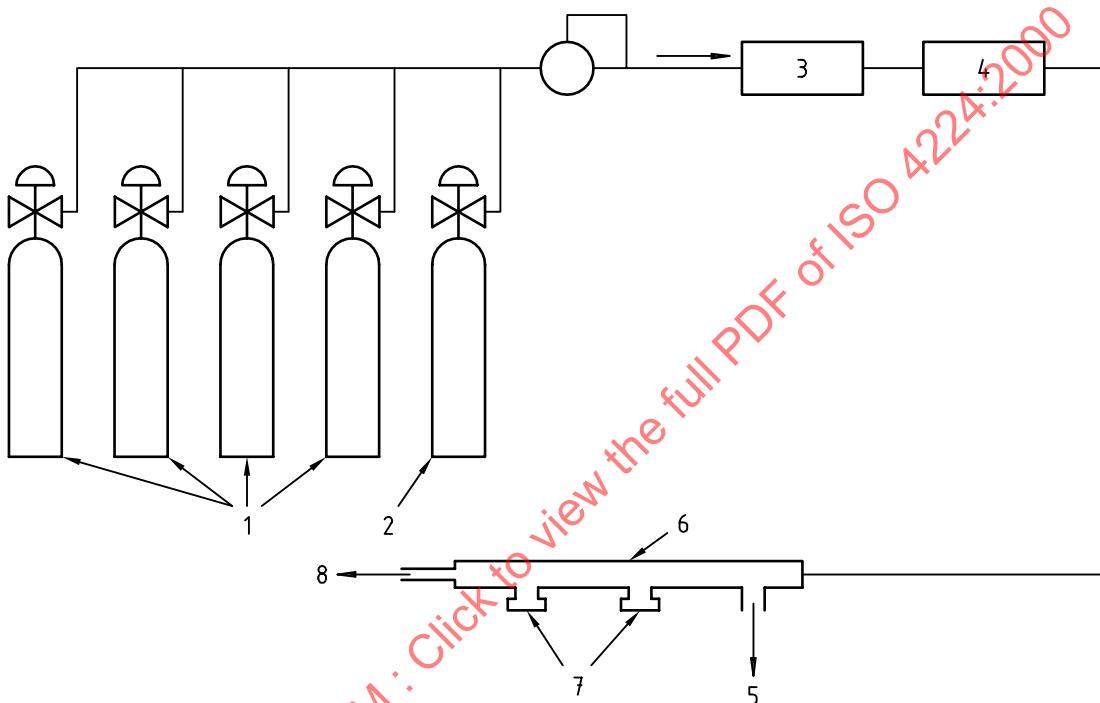
1	Zero-air	6	Extra outlets, capped when not in use
2	Flow controller	7	Output manifold
3	Flowmeter	8	Vent
4	Mixing chamber	9	CO STD
5	To analyser being calibrated		

Figure B.1 — Dilution method for calibration

B.1.2.2 Procedure using multiple cylinders method

Use the procedure for the dynamic dilution method, with the following changes.

- Use a multicylinder system such as the typical one shown in Figure B.2.
- The flow meter need not be accurately calibrated, provided the flow in the output manifold exceeds the analyser flow demand.
- Obtain the various CO calibration concentrations required in B.1.2.1, steps f) and g), without dilution, by selecting the appropriate certified standard cylinder.



Key

1 CO STD	5 To analyser being calibrated
2 Zero-air	6 Output manifold
3 Flow controller	7 Extra outlets capped, when not in use
4 Flowmeter	8 Vent

Figure B.2 — Multiple cylinder calibration

B.2 Zero and span calibration procedures

Carry out the procedure in B.1.1.

Allow the analyser to sample the 80 % span gas until a stable trace is obtained, or for five times the response time, whichever is greater. Mark the reading as "unadjusted span." Do not make any adjustments to zero or span.

Allow the analyser to sample the zero-gas until a stable trace is obtained, or for five times the response time, whichever is greater. Mark the reading as "unadjusted zero".

Adjust the zero control until the trace corresponds to the true zero-gas setting. Mark the trace as "adjusted zero."