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STANDARD

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Ambient air — Determination of the mass concentration of carbon monoxide — Gas chromatographic method

Air ambiant — Détermination de la concentration en masse du monoxyde de carbone — Méthode par chromatographie en phase gazeuse

Reference number
ISO 8186 : 1989 (E)

Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 8186 was prepared by Technical Committee ISO/TC 146, *Air quality.*

Annexes A and B form an integral part of this International Standard. Annex C is for information only.

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Introduction

This International Standard originated from international demands for air pollution research and control.

The method in general can be used for the manual or automatic measurement of carbon monoxide over a wide range of concentrations found in air samples from a variety of sources. This International Standard, utilizing gas chromatography, is applicable to the measurement of low mass concentrations of carbon monoxide in ambient air and for situations where more accuracy, i.e. 5 % or better of the full scale in the ranges of 0 to 1 mg/m^3 and 0 to 25 mg/m^3 is required.

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Ambient air — Determination of the mass concentration of carbon monoxide — Gas chromatographic method

1 Scope

This International Standard specifies a gas chromatographic method for the determination of the mass concentration of carbon monoxide in ambient air from a variety of sources. The method is free from interference because the appropriate gas chromatographic conditions are used to separate the carbon monoxide from all the other constituents in the air sample, before the carbon monoxide is measured. It is intended for the measurement of carbon monoxide at concentrations less than 25 mg/m^3 although it can be successfully applied to concentrations up to 1 000 mg/m^3 respectively[1] at 25 °C and 101,3 kPa. Measurements of carbon monoxide at concentrations of less than 1 mg/m^3 can be obtained with careful operation. The automatic technique is continuous only insofar as several discrete air samples can be drawn and analysed each hour.

NOTE — Although this International Standard is written for two ranges, i.e. 0 to 1 mg/m^3 and 0 to 25 mg/m^3, an intermediate range, e.g. 0 to 10 mg/m^3, could be utilized to advantage if all the concentrations fall within the expected range and more accuracy is desired. It is dependent on the error in reading the output trace.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards listed below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 6143 : 1981, *Gas analysis — Determination of composition of calibration gas mixtures — Comparison methods.*

ISO 6144 : 1981, *Gas analysis — Preparation of calibration gas mixtures — Static volumetric methods.*

3 Principle

Passage of a fixed volume of the air sample through a chromatographic column for effective separation of carbon monoxide from other gaseous constituents. Reduction of the separated carbon monoxide to methane by the hydrogen carrier gas by passage over a heated nickel catalyst (other catalysts and promoters may be used). Passage of the resulting methane through a flame ionization detector. The output signal is proportional to the amount of carbon monoxide present in the sample.

4 Materials

4.1 Gases

See ISO 6143 and ISO 6144. The gases required for the operation of the gas chromatograph shall not contain impurities that will give a signal equal to or more than the minimum detectable carbon monoxide concentration.

Their maximum moisture content shall be less than 10 mg/m^3, total hydrocarbons expressed as methane shall be less than 0,1 mg/m^3 and carbon monoxide shall be less than 0,1 mg/m^3.

WARNING — When using compressed gases, the safety precautions recommended by the supplier shall be followed. In particular, handle methane and hydrogen with care because they present a fire hazard under certain conditions.

4.1.1 Hydrogen is used as the carrier gas in the gas chromatographic separation, for the catalytic reduction of carbon monoxide to methane and for the operation of the flame ionization detector.

4.1.2 Air is required for the operation of the flame ionization detector.

4.1.3 Nitrogen.

4.1.4 Helium.

For certain burners, nitrogen or helium or a mixture of both is added to the fuel gas to optimize sensitivity and stability.

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[1] At the temperature and pressure given, the following conversion factors apply :

1 mg/m^3 ≙ 0,88 ppm (V/V)

1 ppm (V/V) ≙ 1,14 mg/m^3

4.2 Calibration gas mixtures

4.2.1 Methane in air

A certified standard mixture of methane in air is required for measuring the converter efficiency. Its concentration shall be known to within 1 % and be close to that of the highest carbon monoxide standard mixture to be used for calibration.

The converter efficiency is found by comparing the areas of peaks obtained from the known methane gas mixture and the known carbon monoxide gas mixture. The areas of the peaks are in the same ratio as the methane and carbon monoxide concentrations, if complete conversion of the carbon monoxide has been accomplished.

4.2.2 Carbon monoxide in air

Certified standard mixtures of carbon monoxide in air or nitrogen (certified accurate to ± 1 % of component) are used as calibration gases. At least four different concentrations covering the range of measurements being made shall be used, e.g. concentrations of 0, 20 %, 50 % and 80 % of the full scale.

4.3 Converter and gas chromatographic materials

The nickel nitrate hexahydrate used for preparation of the converter column shall be of reagent grade. The converter packing consists of 0,125 mm to 0,15 mm (100 to 120 mesh ASTM) diatomaceous earth (also known as kieselguhr firebrick Chromosorb P 1); diatomaceous earth-pink; diatomaceous earth-firebrick).

The gas chromatographic column material is 0,18 mm to 0,25 mm (60 to 80 mesh ASTM) synthetic alkali metal aluminosilicate beads (may be known as molecular sieve 5A 1) or Zeolox sieve 5A 1)).

If other mesh sizes are used, their equivalency shall be demonstrated.

5 Apparatus

A gas chromatographic system with a flame ionization detector (FID) shall be used. An automatic sampling and injection system provides a series of discrete samples and analyses.

The range of the instrument being used shall be compatible with the concentration of gas to be measured.

5.1 Column

A gas chromatographic column system shall be used to separate carbon monoxide from other components present in the sample. It is important that water is not permanently retained by the packing materials. Hence the column shall be back-flushed between sample injections.

The system recommended in this International Standard does not use a stripper column and works satisfactorily under the conditions recommended. The separated carbon monoxide is passed to the converter and the column is back-flushed in preparation for the next sample.

NOTES

1 Some systems utilize a stripper column that separates the fast-eluting components (methane and carbon monoxide) from the slower-eluting components (carbon dioxide, water and hydrocarbons). After elution of methane and carbon monoxide, the stripper column is switched and back-flushed to remove the slower eluting components.

2 Various packing materials and column dimensions may be used to achieve the required separation (columns are available commercially). A 3,2 mm outer diameter stainless steel tube (copper tube is not recommended) packed with 0,18 mm to 0,25 mm (60 to 80 mesh ASTM) molecular sieve 5A and operated at a temperature above 45 °C is recommended. (The tolerance in the isothermal temperatures recommended throughout this International Standard is ± 5 °C unless otherwise specified.) The column length must be determined by the carrier gas flow applicable to the gas chromatograph being used. For example, a carrier gas flow of 20 cm/min will require a column 2 m long, operated at 45 °C, to give adequate separation.

5.2 Converter

Carbon monoxide is converted to methane by reaction with hydrogen in the presence of a heated nickel catalyst. The reduction occurs according to the following equation :

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

NOTE — Added promoters, such as thorium oxide or ruthenium, have been used[1] to extend the life of the nickel catalyst, especially when higher converter temperatures are used and when carbon dioxide is also being converted to methane. Experience with the procedures recommended in this International Standard has shown that the conversion efficiency of carbon monoxide to methane and the life of the nickel catalyst were not a problem, since small quantities of carbon monoxide were being converted to methane in the presence of pure hydrogen at a relatively low temperature, i.e. 260 °C.

5.3 Converter-oven assembly

Various designs for the heater are available, or it can be constructed in a machine-shop. A suitable arrangement may be constructed from an aluminium block as shown in figure 1. The 100 W cartridge heater with a stainless steel sheath and controlled by a rheostat will provide sufficient heat and stability for the system. The converter tube and the block assembly are wrapped in a suitable insulating material. A thermometer is inserted into the oven block and the desired temperature is reached by manual setting of the rheostat. A temperature of 260 °C has been found to be satisfactory for the conversion of carbon monoxide to methane and avoids problems of tailing and interference from oxygen[2,3].

5.4 Sampling system

A sample injection valve with a sampling loop that has the desired capacity is used to introduce the sample into the gas

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1) Chromosorb P, molecular sieve 5A, Zeolox sieve 5A are examples of suitable products available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of these products.

chromatographic system. A small pump capable of drawing approximately 100 cm^3/min of air through the loop is used to collect the sample.

NOTE 1 — The sampling loop of the injection valve can be readily constructed from 3,2 mm outer diameter stainless steel tubing to give a capacity of approximately 4 cm^3 [4]. Condensation in the sampling loop can be avoided by holding the loop at a constant temperature slightly above sample temperature.

Use a suitable arrangement of sampling valves, such as shown in figure 2, to perform the following sequence of functions :

a) By-pass configuration. The carrier gas flow is split into two equal streams by means of needle valves. One portion flows through valve 4 and the converter to the detector, the other flows through valves 1, 2 and 3, back-flushing the column, and then through valve 4 to the detector. During this mode, the sampling pump is turned on to flush and fill the sample loop.

b) Inject configuration. In this mode the carrier gas flow previously passing through the converter is diverted directly to the detector by valve 4. The other stream of carrier gas is diverted through the sampling loop by switching valve 1, and then passes directly through the column by switching valves 2 and 3. Valve 4 then allows the carrier gas stream to flow through the converter to the detector. Immediately after the converted methane has passed through the detector, the system is reverted to by-pass mode, allowing for back-flushing of the column and refilling of the sampling loop.

Use timers and valve actuators to control the sequence of operation and allow a series of discrete samples to be analysed. The recording device can also be timed to operate only during elution of the converted carbon monoxide. The time required for one cycle is dependent on the back-flushing needed to clean the column before injection of the next sample. With the system described, it should be possible to process up to 10 samples per hour.

NOTE 2 — Contamination of the gas chromatographic column by water vapour will change the retention time of the carbon monoxide and may require adjustment of the timing sequence. The line between the converter and detector should be as short as possible and held at a temperature above 100 °C to prevent condensation of water.

Dimensions in millimetres

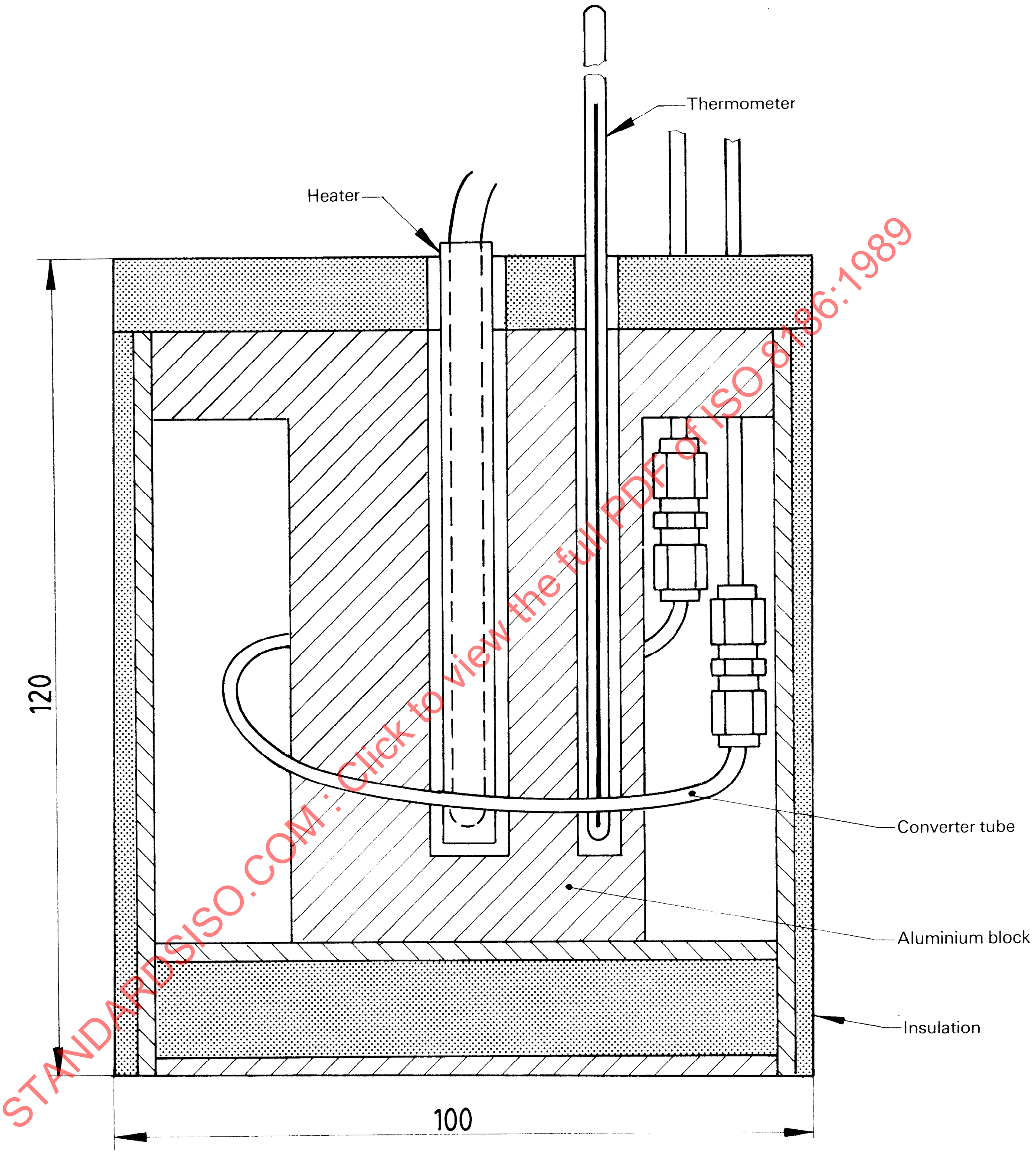

Figure 1 — Arrangement for the converter

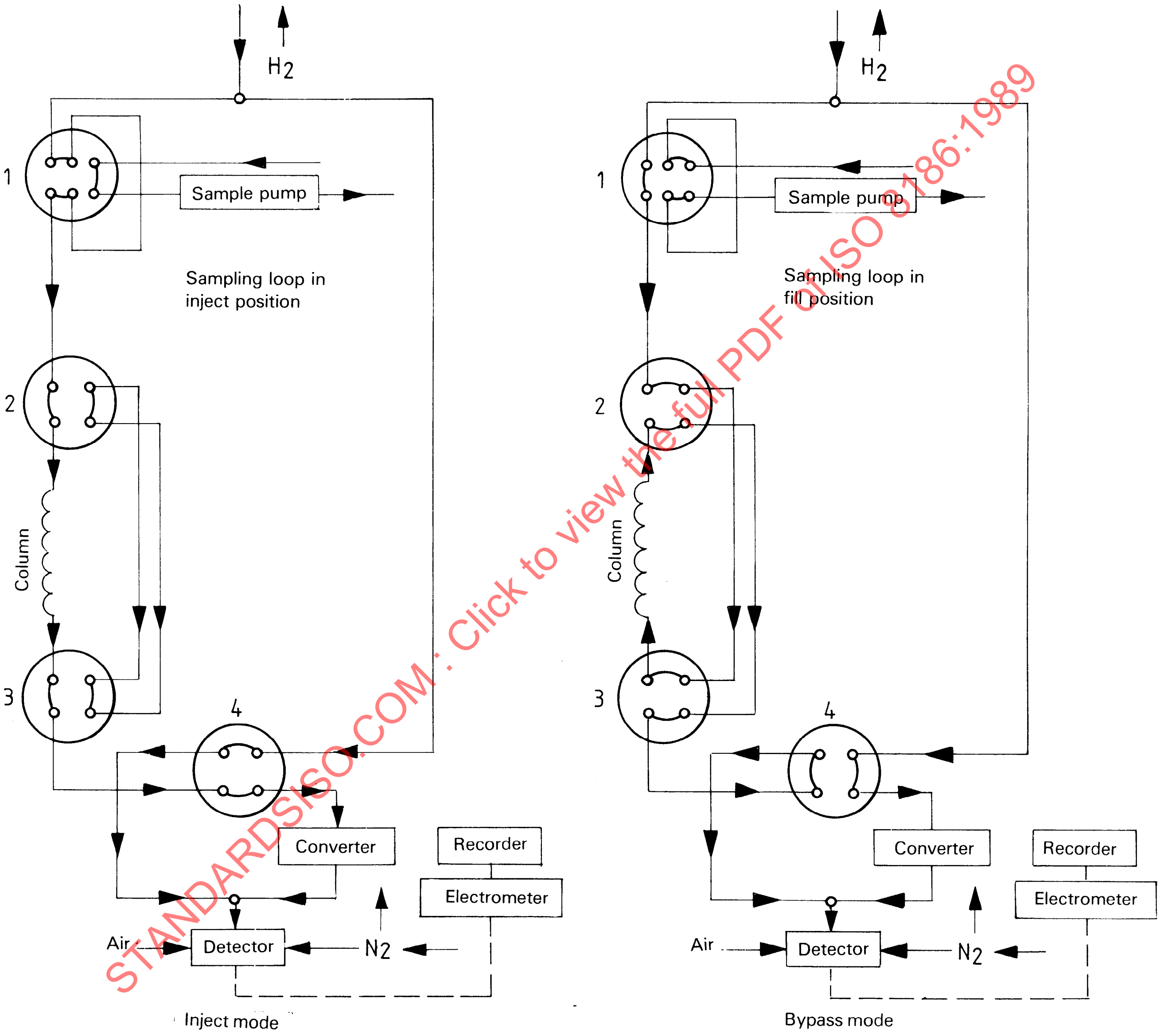

Figure 2 — Arrangement for gas flowing

6 Procedure

The following features shall be considered in the measurement of carbon monoxide :

- the range within which the concentrations are expected to fall;
- the output signal and the minimum concentration detectable above the noise signal;
- the number of discrete samples to be taken per unit time;
- the zero and span drift;
- the repeatability of measurements;
- the efficiency of the converter;
- the range of temperature over which the samples will be taken.

Such considerations will enable the selection of operating parameters that will provide the best estimate of the carbon monoxide concentrations under study.

6.1 Preparation of catalyst

Prepare the catalyst by the following procedure, or by a method yielding an equivalent product.

Add excess nickel nitrate hexahydrate [$Ni(NO_3)_2.6H_2O$] to 25 ml of distilled water at room temperature (20 °C ± 2 °C). Filter off the undissolved nickel nitrate and soak 10 g of 0,125 mm to 0,15 mm (100 to 120 mesh ASTM) diatomaceous earth in the saturated nickel nitrate solution. Filter under vacuum and dry the residue overnight at 110 °C. Finally, heat in air for 5 h at 500 °C.

6.2 Preparation of converter tube

Prepare the converter tube by packing a stainless steel tube with diatomaceous earth treated with nickel nitrate (6.1).

NOTE 1 — Suitable tubing is 120 mm long with an internal diameter of 1,6 mm and an outer diameter of 3,2 mm.

Enclose the converter tube in a heater or small temperature-controlled oven, capable of maintaining a steady temperature of 260 °C (see 5.3).

NOTE 2 — Complete converter tubes may also be obtained commercially.

6.3 Conditioning of converter

Assemble the sampling, converter and gas chromatographic system as shown in figure 2.

Adjust the system so that it operates continuously in the by-pass mode. The automatic switching is rendered inoperative during this operation. The recorder may also be switched off during this conditioning period. Turn on the gas chromatograph and adjust as directed in the manufacturer's operating instructions.

Adjust the converter reactor temperature to 350 °C and operate the system for about 10 h to reduce the deposited nickel oxide to the metallic state.

6.4 Establishing the baseline and retention time

Assemble the sampling, converter and gas chromatographic system as shown in figure 2. Adjust the system in the by-pass mode. The automatic switching is rendered inoperative during this operation.

Turn on the gas chromatograph and adjust as directed in the manufacturer's operating instructions.

Turn on the converter system and adjust the temperature to 260 °C.

Operate the system long enough for a steady baseline to be achieved.

Turn on the sampling pump and connect a calibration gas mixture, which falls within the range to be used, to the inlet sampling port.

Manually switch the system from the by-pass mode to the inject mode (see figure 2). Note the time elapsed from the injection of the sample to the completion of the carbon monoxide trace.

Reactivate the automatic switching system and adjust the sampling system so that the instrument is in the inject mode (see figure 2) for the elapsed time noted above. The instrument should operate in the by-pass mode longer than in the inject mode to provide effective back-flushing of the chromatographic column.

6.5 Preparation of calibration curve

Prepare a calibration curve in the following manner.

Select the range, i.e. 0 to 1 mg/m^3 or 0 to 25 mg/m^3 of carbon monoxide, and establish the carrier gas baseline as follows :

Connect the inlet sample port to a zero air supply. Use a warm-up time long enough to allow a steady baseline to be achieved. Connect the calibration gas mixture which is near the upper end of the range to be used, to the inlet sampling port. Repeat this and the previous steps until adjustments are no longer required.

Use at least four calibration gas mixtures (4.2), including zero air, that cover the range being measured, to determine the calibration curve.

Attach each calibration gas container in turn to the input of the sample loop. Allow each gas to flow until the sample loop is completely flushed of any previous sample and is completely filled with the desired gas. Allow the gas to come to ambient pressure and inject. Activate the analytical system so that the carbon monoxide content of the sample in the loop is passed through the gas chromatographic column and converter to the detector. Analyse at least three samples of each calibration gas mixture to assure repeatability and reliability.

NOTE — The peak areas obtained from the calibration gas mixtures are used to prepare a calibration curve, which is normally linear. Peak height measurements can usually be used for routine analyses without loss of accuracy (see annex B).

6.6 Converter efficiency

Use methane in air (4.2.1) to measure converter efficiency. The concentration of methane shall be at the high end of the carbon monoxide range of measurements.

This methane misture is sampled and the resulting peak is compared to a peak area for a carbon monoxide calibration gas mixture of similar concentration. The ratio of peak areas measured shall be similar to the methane and carbon monoxide concentration ratio. This gives a measure of the converter efficiency, which should be greater than 95 %. If the converter efficiency is constant and known accurately then a value less than 95 % may also be acceptable and allowed for in the calculation. A small adjustment to the converter temperature may be utilized to improve the efficiency. If this adjustment fails to improve the efficiency, then the catalyst may need replacement (see 5.2).

Since the methane peak appears at a time different from that of the methane from the converted carbon monoxide peak, the switching system shall be altered accordingly during the converter efficiency test.

6.7 Determination

Continuously draw sample gas through the loop or its by-pass with the sampling pump. The sample flow rate (approximately 100 cm^3/min) is sufficient to purge and fill the sample loop. At the appropriate time in the sampling programme the contents of the loop are automatically injected into the gas chromatographic system and analysed for carbon monoxide content.

7 Expression of results

Determine the concentrations of carbon monoxide from the comparison of the peak areas (see annex B) obtained from the calibration mixtures and the sample.

NOTE — Carbon monoxide concentrations may be converted from milligrams per cubic metre to parts per million by volume as follows :

At 25 °C and 101,3 kPa,

$$1 \text{ ppm } (V/V) \mathrel{\hat{=}} 1{,}14 \text{ mg/m}^3$$

At other temperatures, at 101,3 kPa,

$$1 \text{ ppm } (V/V) \mathrel{\hat{=}} 1{,}14 \times \frac{273{,}1 + t}{298{,}1} \text{ mg/m}^3$$

where t is the temperature, in degrees Celsius.

8 Repeatability and accuracy

8.1 Repeatability

A repeatability of 0,05 mg/m^3 at 1 mg/m^3 of carbon monoxide is attainable and is primarily a function of the flow rates of hydrogen, nitrogen and air used.

8.2 Accuracy

The accuracy of the method is estimated to be better than ± 5 % of full scale, i.e. 0,05 mg/m^3 in the range 0 to 1 mg/m^3 of carbon monoxide and ± 1,25 mg/m^3 in the range 0 to 25 mg/m^3 of carbon monoxide.

NOTE — 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 determined in the calibration gas mixtures.

9 Test report

The test report shall include the following information :

a) a complete identification of the air sample;

b) a reference to this International Standard;

c) the results;

d) any unusual features noted during the determination.

Annex A
(normative)

Typical performance characteristics for instruments

The values given below are typical performance characteristics and are not to be interpreted as being applicable to any particular instrument.

Measurement range : 0 to 1 mg/m^3 and 0 to 25 mg/m^3 (other ranges possible)

Lower detection limit : 0,05 mg/m^3

Repeatability : 5 % of full scale

Period of unattended operation : about 3 days

Annex B
(normative)

Calculation of concentrations

Concentrations are normally determined from peak areas because the relationship between the two is linear over small ranges (0 to 1 mg/m^3). However the concentration, without loss of accuracy, may be obtained from the peak height, provided the peaks are reasonably sharp without tailing. Since it is simpler to measure peak heights than areas, this is recommended for routine monitoring. One may also refer to ISO 6143.

Annex C
(informative)

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