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Stationary source emissions — Manual method for the determination of the methane concentration using gas chromatography

Émissions de sources fixes — Méthode manuelle pour la détermination de la concentration en méthane par chromatographie en phase gazeuse

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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 2.

The main task of technical committees is to prepare International Standards. 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 document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 25139 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 1, *Stationary source emissions*.

Introduction

Methane (CH_4) is a gas of relevance to the climate ("greenhouse gas") and contributes directly to the atmospheric greenhouse effect. The emissions of methane originate from natural sources and those due to human activity. Significant sources are, for example, cattle breeding, cultivation of rice, extraction and transport of natural gas, and landfills. Other important sources contributing to emissions of methane are, for example, composting plants, the use of biogas and natural gas, and biomass firings. This International Standard specifies a method of measurement for the determination of methane emissions from stationary sources.

Stationary source emissions — Manual method for the determination of the methane concentration using gas chromatography

1   Scope

This International Standard specifies a manual method for the determination of the concentration of methane emissions from stationary sources.

This International Standard specifies an independent method of measurement, which is validated for mass concentrations up to 1 500 mg/m^3.

NOTE 1   An independent method of measurement is used for such purposes as calibration or validation of permanently installed measuring systems.

NOTE 2   An "independent method of measurement" is termed "standard reference method (SRM)" in EN 14181[5].

2   Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 9169, *Air quality — Definition and determination of performance characteristics of an automatic measuring system*

EN 15267-3, *Air quality — Certification of automated measuring systems — Part 3: Performance criteria and test procedures for automated measuring systems for monitoring emissions from stationary sources*

3   Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
reference gas
⟨air quality⟩ gas of known, reliable and stable composition

NOTE   In the context of this International Standard, a reference gas is used to calibrate the gas chromatograph.

3.2
interferent
interfering substance
⟨air quality⟩ substance present in the air mass under investigation, other than the measurand, that affects the response

[ISO 9169:2006, 2.1.12]

3.3
mass concentration
⟨stationary source emissions⟩ concentration of a substance in an emitted waste gas expressed as mass per volume

NOTE   Mass concentration is often expressed in milligrams per cubic metre.

[ISO 25140:2010[3], 3.14]

3.4
uncertainty (of measurement)
parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand

[ISO/IEC Guide 98-3:2008[4], 2.2.3]

3.5
standard uncertainty
uncertainty of the result of a measurement expressed as a standard deviation

[ISO/IEC Guide 98-3:2008[4], 2.3.1]

4   Symbols and abbreviated terms

AMS   automatic measuring system

FID   flame ionization detector

FKM   fluoro rubber

GC   gas chromatograph

PE   polyethylene

PET   poly(ethylene terephthalate)

PLOT   porous layer open tubular

PTFE   polytetrafluoroethylene

QA/QC   quality assurance and quality control

A peak area

e_j residual at mass concentration level γ_j

f_{GC} GC calibration factor

k slope of the calibration line

L limit of detection

$m_{H_2O,v}$ mass of water vapour

M_{CH_4} molecular mass of methane (16 g/mol)

M_{H_2O}	molecular mass of water (18 g/mol)
n	number of measurements
s_r	repeatability standard deviation
S_{GC}	GC signal
$S_{GC,cal}$	GC signal in response to the reference gas applied
V_0	volume of the dry gas sampled
V_m	standard molar volume (22,4 l/mol)
x_i	ith measured value
$\bar{x}$	average of the measured values x_i
$\bar{x}_j$	average of the measured values at mass concentration level γ_j
$\gamma_{CH_4,s}$	methane mass concentration at standard conditions of temperature and pressure
$\gamma_{CH_4,(H_2O)_0}$	methane mass concentration at reference conditions of water vapour (dry gas)
γ_{CH_4,O_2}	methane mass concentration at reference conditions of oxygen
γ_j	jth mass concentration level
$\rho_{H_2O,v}$	density of water vapour
$\varphi_{CH_4,cal}$	methane content, as a volume fraction, of the reference gas applied during calibration
$\varphi_{CH_4,o}$	methane content, as a volume fraction, at operating conditions
φ_{H_2O}	water vapour content, as a volume fraction, in the waste gas
$\varphi_{O_2,m}$	measured oxygen content, as a volume fraction, in the waste gas
$\varphi_{O_2,ref}$	reference oxygen content, as a volume fraction

5   Principle

The sample gas is extracted from the waste gas duct via a sampling system and pumped into a gas-sampling bag or canister. A portion of the sample is taken off from the gas-sampling bag or canister and introduced into a gas chromatographic system. After separation on a packed or capillary column, methane is determined by means of a flame ionization detector.

6 Equipment

6.1 Sampling system

The sampling system shall allow for the extraction of the sample gas from the waste gas duct. It consists in principle of:

— sampling probe;

— particle filter;

— sample gas cooler;

— sample gas flow meter;

— sample gas pump;

— vacuum pump, if necessary;

— gas-sampling vessel (bag, glass tube or canister), or direct sampling loop to the GC.

Several sampling techniques are suitable such as:

— use of gas-sampling bags with upstream pump (see Figure 1);

— use of evacuated gas-sampling vessels made of glass or canisters made of corrosion-resistant materials (e.g. stainless steel) with upstream pump (see Figure 2);

— use of the "lung principle" with the gas-sampling bag placed in an evacuated container;

— use of a sampling system as shown in Figure 1 but with the gas-sampling bag replaced by a sampling line directly connected to the loop sampling system of the GC.

Key
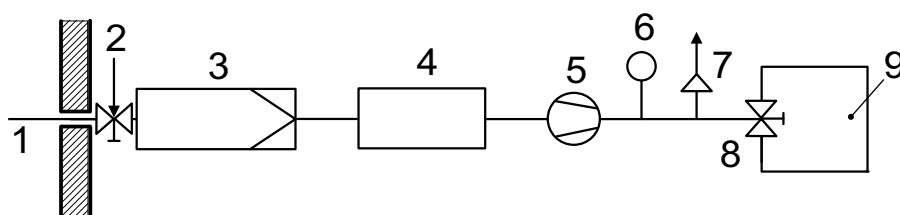
1	sampling probe, heated (if necessary)	6	flow meter
2	valve for introducing test gases	7	bypass valve for purging the sampling system
3	particle filter, heated	8	sampling bag valve
4	sample gas cooler or permeation dryer	9	gas-sampling bag
5	sample gas pump		

Figure 1 — Example of a sampling system with gas-sampling bag

Key
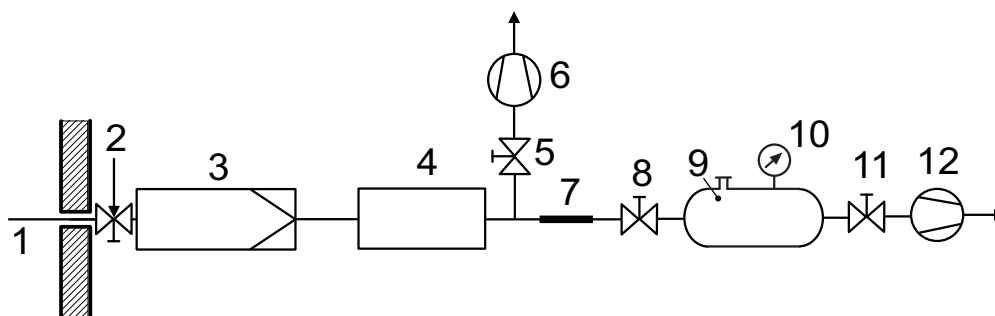
1	sampling probe, heated (if necessary)	7	throttle element
2	valve for introducing test gases	8	shut-off valve
3	particle filter, heated	9	gas-sampling vessel or canister
4	sample gas cooler or permeation dryer	10	temperature and pressure measuring device
5	control valve	11	shut-off valve
6	sample gas pump	12	vacuum pump (if necessary)

Figure 2 — Example of a sampling system with evacuated gas-sampling vessel

The sampling line shall be as short as possible. The sampling line shall be installed so as to descend to the cooler. Condensation shall be avoided at any point of the sampling system.

The sampling system shall meet the following requirements:

— the sampling probe shall be a tube made of stainless steel or glass, which can be heated to 150 °C, if necessary, equipped with a device (e.g. a valve) for introducing test gases;

— the dust filter shall be a quartz fibre or ceramic filter in a filter housing and shall be heatable to 150 °C, if necessary;

— the sampling line shall be made of stainless steel or polytetrafluoroethylene (PTFE) and shall be heatable to 150 °C, if necessary;

— the sample gas cooler or permeation dryer shall be suitable for a flow rate up to 1 l/min;

— the sample gas pump shall be gas-tight with adjustable flow rate (up to 1 l/min), and shall be heatable, if necessary;

— vacuum pump for evacuating the gas-sampling vessel down to a residual pressure of 10 hPa to 20 hPa;

— connecting pieces for components of the sampling apparatus shall be made of an inert tubing material, e.g. PTFE or fluoro rubber (FKM);

— the flow meter with control valve shall be suitable for measuring the sampling flow rate;

— the gas-sampling vessel shall be gas-tight (e.g. a plastic bag with closable filler nozzle or canister of corrosion-resistant materials equipped with valves) with a volume of 5 l to 30 l;

— all components of the sampling system shall be made of corrosion-resistant material;

— all components upstream the cooler shall withstand a temperature of 150 °C, if necessary.

Suitable materials for the storage of methane samples are aluminium-coated polyethylene (PE) and poly(vinyl fluoride). Sample storage in gas-sampling bags made from these materials for at most 10 days is possible without significant methane losses, in aluminium-coated PE bags even longer.

When using poly(ethylene terephthalate) (PET) bags, which are usually taken for odour sampling, storage should not exceed 2 days. Longer storage results in significant losses of methane (Reference [6]).

CAUTION — The use of gas-sampling bags which are made from pure polyethylene is not recommended as methane diffuses out and ambient air diffuses in.

The gas-sampling vessel should be equipped with a septum or a valve depending on the GC injection technique (gas-tight syringe or sample loop).

6.2   Analytical apparatus

The analytical apparatus consists of the following components, which shall meet the specified requirements:

— gas chromatograph (GC) with flame ionization detector (FID), which shall be equipped with a sample injection with gas sample loop or split injector;

— separation column, which shall be a packed column or capillary column;

— injection syringe, if necessary, which shall be gas-tight and should be suitable for a volume, for example, of 1 ml;

— GC signal output, which can be equipped with a data evaluation unit.

7   Measurement procedure

7.1   General

Comprehensive measurement planning shall be performed before the measurement, taking into consideration the specific measurement task.

7.2   Sampling

7.2.1   Preparation

The sampling equipment shall be cleaned, prepared, and analytically checked before transporting to the site.

The gas-sampling bags are used, they shall be cleaned before sampling by purging with nitrogen followed by a complete removal of the purging gas. The purge and removal of the sampling bag with nitrogen shall be repeated at least three times to ensure the cleanliness of the bag. After the last purging, the gas removed and analysed shall give a signal below the limit of detection.

7.2.2   Sampling procedure

7.2.2.1   General

The sampling equipment shall be assembled and checked for possible leaks by sealing the entry nozzle and starting the suction device. The leak flow, for example measured by pressure variation after evacuation of the train at the maximal low-pressure reached during sampling, shall be below 2 % of the sampling flow rate.

Sampling shall be performed according to the sampling technique selected from 7.2.2.2 to 7.2.2.5.

7.2.2.2   Bag sampling according to Figure 1

The sampling probe shall be inserted into the waste gas duct and the sampling system purged with waste gas through the sampling probe, the particle filter and the sample gas cooler by starting the pump and by use of the bypass for a sufficient time period.

Afterwards, a partial flow of the waste gas is pumped into the gas-sampling bag by opening the sampling bag valve.

7.2.2.3   Evacuated vessel or canister according to Figure 2

The sampling probe shall be inserted into the waste gas duct and the sampling system purged with waste gas through the sampling probe, the particle filter and the sample gas cooler by starting the pump and by use of the bypass. At the same time, the gas vessel or canister shall be evacuated by use of the vacuum pump. The evacuation is completed at a residual pressure which corresponds to the water vapour partial pressure at the temperature of the vessel.

NOTE   The water vapour partial pressure is approximately 12 hPa at 10 °C, and approximately 42 hPa at 30 °C.

After the evacuation, an equilibrium pressure is reached in the gas collection vessel; read this off the manometer and note it in the sampling record. Likewise, note the temperature of the gas collection vessel (usually ambient temperature). Then check the vessel for gas-tightness: it is gas-tight if the equilibrium pressure remains stable over a period of approximately 1 min. If not, there may be a leak in the gas collection vessel. It is then necessary either to make this vessel gas-tight or to reject it.

Open the inlet valve of the gas-sampling vessel and take the sample gas from the passing sample gas flow via the throttle element.

The throttle element used shall be designed in such a manner that, in the sampling period, the internal pressure of the gas collection vessel rises to a full pressure of 400 hPa to 500 hPa.

When the full pressure has been achieved, terminate sampling by closing the inlet valve. After approximately 5 min (temperature equilibration) determine and record the internal pressure and the temperature of the gas-sampling vessel.

7.2.2.4   Lung principle

Using the "lung principle", the sample bag is placed in a rigid container, the air is removed from the container using a vacuum pump, the under pressure in the container causes the bag to fill with a volume of sample equal to that which has been removed from the container. The sampling bag can be connected directly to the sampling probe. Condensation can be avoided by partly prefilling the bag with synthetic air.

7.2.2.5   Direct connection to the loop sampling system of the GC

Proceed in accordance with 7.2.2.2 if the sampling bag is replaced by a sampling line directly connected to the loop sampling system of the GC. In this case, the sample volume need not be determined since the concentration is measured directly.

7.2.2.6   Sampling period

The sampling period shall be chosen according to the measurement objective.

NOTE   Typical sampling periods are in the range 10 min to 60 min. The sampling period can be varied by controlling the filling rate or the volume of the gas-sampling vessel.

On completion of sampling, the filler nozzle of the gas-sampling bag shall be closed.

7.3 Analytical determination

7.3.1 Injection with sample loop

The gas-sampling bag shall be connected to the sample loop of the GC by tubing whose length is as short as possible. A sufficiently large volume shall be aspirated or forced through the sample loop; allow sufficient time for equilibration to ambient pressure. Then the loop contents shall be ejected into the carrier gas flow. The compounds of the sample are separated on the column and the FID signal shall be recorded by the data evaluation unit.

7.3.2 Injection with gas-tight syringe

The cannula of the syringe shall be pierced through the septum of the gas-sampling bag and the syringe shall be filled with sample gas by repeated movement of the piston of at least 10 times. The sample gas shall then be injected into the GC without delay. In order to achieve reproducible results, the cannula should remain in the injector for a defined time (e.g. 3 s) after injection.

7.3.3 Typical GC parameters

Table 1 shows typical GC parameters.

Table 1 — Typical GC parameters

Column:	thickfilm capillary, silica PLOT (porous layer open tubular), 30 m, 0,32 mm inner diameter
GC:	oven: 50 °C, isotherm
Split:	approx. 10:1; 15 ml/min
Injector temperature:	150 °C[a]
FID temperature:	250 °C
Carrier gas:	nitrogen
Flow rate of carrier gas:	1,56 ml/min
Sample volume:	500 µl, variable
Retention time (methane):	1,97 min
[a] The high injector temperature is necessary to keep higher boiling point hydrocarbons in the gas phase to avoid contamination in the system.	

7.4 Interferents

Methane shall be separated from other hydrocarbons and oxygen on the GC column. A strict baseline separation at least from ethane is necessary.

8 Calculation of the results

Results of the measurement shall be expressed as mass concentrations at reference conditions (dry gas) and oxygen content, if required.

From the GC signal, the methane volume fraction, $\varphi_{CH_4,o}$ at operating conditions is calculated by Equation (1):

$$\varphi_{CH_4,o} = f_{GC} \cdot S_{GC} \tag{1}$$

where

f_{GC} is the GC calibration factor;

S_{GC} is the GC signal, in counts.

The GC calibration factor, f_{GC}, is determined in the laboratory with known methane volume fractions according to Equation (2):

$$f_{GC} = \frac{\varphi_{CH_4,cal}}{S_{GC,cal}}$$ (2)

where

$\varphi_{CH_4,cal}$ is the methane volume fraction of the reference gas applied during calibration;

$S_{GC,cal}$ is the GC signal, in counts, in response to the reference gas applied.

If the methane concentration is provided as a volume fraction from the GC analysis, Equation (3) shall be used to calculate the mass concentration, $\gamma_{CH_4,s}$, at standard conditions of temperature and pressure (273 K, 1 013 hPa):

$$\gamma_{CH_4,s} = \varphi_{CH_4,o} \cdot \frac{M_{CH_4}}{V_m}$$ (3)

where

$\varphi_{CH_4,o}$ is the methane volume fraction at operating conditions;

M_{CH_4} is the molecular mass of methane (16 g/mol);

V_m is the standard molar volume (22,4 l/mol).

If necessary, the measured methane concentration shall be corrected to reference conditions of water vapour (dry gas) using Equation (4):

$$\gamma_{CH_4,(H_2O)_0} = \gamma_{CH_4,s} \cdot \left(\frac{100\ \%}{100\ \% - \varphi_{H_2O}} \right)$$ (4)

where

$\gamma_{CH_4,s}$ is the mass concentration of methane at standard conditions;

φ_{H_2O} is the water vapour content, as a volume fraction expressed as a percentage, in the waste gas (waste gas humidity).

If the water vapour content is determined as mass concentration, Equation (5) shall be used to calculate the water vapour content, φ_{H_2O}, as a volume fraction, in the waste gas:

$$\varphi_{H_2O} = \frac{m_{H_2O,v} / \rho_{H_2O,v}}{\left(m_{H_2O,v} / \rho_{H_2O,v} \right) + V_0}$$ (5)

where

$m_{H_2O,v}$ is the mass of water vapour;

$\rho_{H_2O,v}$ is the density of water vapour (0,8 g/l or 0,8 kg/m^3), given by

$$\rho_{H_2O,v} = \frac{M_{H_2O}}{V_m}$$

in which M_{H_2O} is the molecular mass of water (18 g/mol);

V_0 is the volume of the dry gas sampled.

If necessary, the measured methane concentration at standard conditions of temperature and pressure, $\gamma_{CH_4,s}$, shall be corrected to reference conditions of oxygen using Equation (6):

$$\gamma_{CH_4,O_2} = \gamma_{CH_4,s} \cdot \left(\frac{21\% - \varphi_{O_2,ref}}{21\% - \varphi_{O_2,m}} \right) \qquad (6)$$

where

γ_{CH_4,O_2} is the methane mass concentration at reference conditions of oxygen;

$\varphi_{O_2,m}$ is the measured oxygen content, as a volume fraction expressed as a percentage, in the waste gas;

$\varphi_{O_2,ref}$ is the reference oxygen content, as a volume fraction expressed as a percentage.

9   Quality assurance and quality control procedures

9.1   General

QA/QC is important in order to ensure that the uncertainty of the measured values for methane is kept within the limits specified for the measurement task.

NOTE   Procedures for the determination of the uncertainty of measured values are specified in, for example, ISO/IEC Guide 98-3[4] and ISO 20988[2].

Measuring devices used in the laboratory are usually covered by internal QA/QC procedures of the laboratory. In addition, the checks specified in 9.3 have to be performed with a frequency and with the criteria specified in 9.2.

9.2   Criteria and frequency of checks

Table 2 shows the minimum frequency of checks. The user shall implement the relevant standards for determination of performance characteristics or procedures described in Annex B.

Table 2 — Minimum frequency of checks for quality assurance and quality control during the operation

Check	Requirement	Minimum frequency
Calibration of the GC	use of CH_4 reference gas of at least five different concentrations	once per analysing day
Lack of fit of the calibration function	$\leqslant 2$ % of the value of the reference gas applied at any point of the GC calibration curve referred to the average value at that point	once per analysing day
Limit of detection	$\leqslant 2,0$ mg/m^3 (0 °C, 1 013 hPa)	after each change of GC conditions (as part of lack of fit test)
Repeatability standard deviation of the GC at span point	$\leqslant 2$ % detected at span point	after each change of GC conditions
Separation efficiency	baseline separation between methane and ethane	after each change of GC conditions
Sampling system	cleanliness and leak tightness	before each measurement series and once per working day
Cleaning of particulate filters	—	before each measurement series with a filter change, if needed

The user shall implement a procedure to ensure that the zero gases and test gases used meet the uncertainty requirement specified in Annex A, e.g. by comparison with a reference gas of higher quality.

9.3 Performing the checks

9.3.1 General

The results of the QA/QC procedures shall be documented.

9.3.2 Calibration of the gas chromatograph

The GC shall be calibrated by use of reference gas with at least five different concentrations in accordance with B.1 at least once per analysing day.

9.3.3 Lack of fit of the gas chromatograph

The lack of fit of the response of the GC shall be checked in accordance with B.2 at least once per analysing day.

9.3.4 Limit of detection

The limit of detection shall be checked in accordance with B.3 at least after each change of GC conditions.

9.3.5 Repeatability standard deviation of the gas chromatograph at span point

The repeatability standard deviation of the GC at span point shall be checked in accordance with B.4 at least after each change of GC conditions.

9.3.6 Sampling system

The entire sampling system shall be checked in accordance with B.5 before each sampling series and at least once per working day.

9.3.7 Cleaning or changing of particulate filters

The particulate filter shall be checked at least once for each measurement series and changed if needed. During the filter change, the filter housing shall be cleaned.

9.4 Check of the measurement system

To check the entire measurement system, the whole measurement procedure (sampling, analysis) is carried out using the lowest and highest concentrations of test gas under conditions identical to those during real waste gas-sampling and analysis. This procedure has to be carried out before each measurement series and at least once per working day. For this purpose, the low and high concentration test gases are fed into the sampling system at the sampling probe upstream of the particle filter. The measured values should not differ by more than 5 % from the nominal values of the test gas fed directly into the GC.

10 Performance characteristics

Annex C shows typical performance characteristics of the method of measurement.

11 Test report

The test report shall include at least the following information:

a)   reference to this International Standard (ISO 25139:2011);

b)   description of the purpose of tests;

c)   description of the whole sampling system and the analytical system;

d)   details of the quality and the concentration of the reference gases used;

e)   details of the check of the entire measurement system (at the inlet of the sampling line and at the injection loop of the GC);

f)   description of plant and process;

g)   identification of the sampling plane;

h)   description of the location of the sampling point(s) in the sampling plane;

i)   description of the operating conditions of the plant process;

j)   changes in the plant operations during sampling, e.g. burner load changes;

k)   sampling date, time and duration;

l)   measured values;

m)   measurement uncertainty;

n)   results of any checks;

o)   any deviations from this International Standard.

Annex A
(normative)

Operational gases

A.1 General

A number of operational gases are required when using this International Standard. For all zero and test gases, the carrier gas shall be identical and should be similar to the waste gas composition (waste gas matrix).

A.2 Carrier gas

The carrier gas shall consist of helium, nitrogen or hydrogen with a purity of at least 99,999 % mass fraction.

A.3 Combustion air for the gas chromatograph

The combustion air shall consist of synthetic (hydrocarbon-free) or purified air.

A.4 Fuel gas for the gas chromatograph

The fuel gas usually consists of hydrogen. The purity of the fuel gas used shall be at least 99,999 % mass fraction.

A.5 Test gases

Test gases shall consist of methane in nitrogen or synthetic air. They shall have a known concentration with a maximum permissible expanded uncertainty of 2,0 % of its nominal value traceable to national standards.

The highest test gas concentration should be about 80 % of the selected measuring range. Other concentrations can be provided by dilution.

NOTE   As the uncertainty of the test gas concentration has significant influence on the measured values, test gas concentrations are usually selected to cover the range of the expected methane concentrations on site.

A.6 Reference gas

Reference gas shall consist of methane in nitrogen or synthetic air. It shall have a known concentration with a maximum permissible expanded uncertainty at 95 % confidence of 1,0 % of its nominal value traceable to national standards.

Reference gas shall be provided at a concentration of about 80 % of the selected measuring range.

Annex B
(normative)

Quality assurance and quality control procedures

B.1 Calibration of the gas chromatograph

The calibration of the GC establishes the statistical relationship between values of the peak area indicated by the GC and the corresponding values of the reference gas. The GC is calibrated by introducing methane reference gases of known concentrations into the GC gas sample loop. The concentrations should be 0 %, 20 %, 40 %, 60 % and 80 % of the selected measuring range. The different reference gas concentrations may be prepared, for example, by using gas mixing devices where the concentrated reference gas is diluted with nitrogen.

The calibration function presented in Equation (B.1) is calculated by linear regression of the measured values (peak area) against the methane mass concentrations of the reference gases:

$$A = k \cdot \gamma_{CH_4} \qquad (B.1)$$

where

  A is the peak area;

  k is the slope of the calibration line;

  γ_{CH_4} is the methane mass concentration.

The calibration function shall be linear in the selected measuring range.

B.2 Lack of fit

The lack of fit (linearity) shall be checked in the laboratory by feeding at least five reference gases with concentrations evenly distributed over the selected measuring range. The different gas concentrations may be produced using a dilution system. The maximum expanded uncertainty of the test gas concentrations shall be less than 33 % of the lack of fit criterion.

NOTE   The lack of fit check can be combined with the calibration of the GC.

Perform at least 10 consecutive injections or samplings into the GC for each reference gas with the accepted value γ_j. Determine the residuals e_j (lack of fit) on the basis of a linear regression as specified in ISO 9169 or EN 15267-3. In this test procedure, a regression line is established between the readings of the GC (x values) and the reference gas values (γ values). In the next step, the average $\overline{x}_j$ of the readings at each reference gas level is calculated. Then the deviation (residual) of the average to the corresponding value $\hat{x}_j$ estimated by the regression line shall be determined according to Equation (B.2):

$$e_j = \hat{x}_j - \overline{x}_j \qquad (B.2)$$

The residuals e_j at each test gas concentration shall meet the performance criterion specified in Table 2.

B.3 Repeatability standard deviation near zero point and limit of detection

The limit of detection shall be determined by application of a reference gas near the zero point (lowest concentration of lack of fit test). If the repeatability standard deviation at zero point is determined during the lack of fit test, the reference gas near zero concentration applied during the test shall be used.

The measured values obtained shall be used to determine the repeatability standard deviation near the zero point using Equation (B.3):

$$s_r = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}}$$ (B.3)

where

s_r is the repeatability standard deviation;

x_i is the ith measured value;

$\bar{x}$ is the average of the measured values x_i;

n is the number of measurements, $n = 20$.

The repeatability standard deviation near zero point shall meet the performance criterion specified in Table 2.

The limit of detection L is calculated from the repeatability standard deviation near zero point by Equation (B.4):

$$L = 2s_r$$ (B.4)

B.4 Repeatability standard deviation at span point

The repeatability standard deviation at span point shall be determined by application of a reference gas at one point in the upper range of the GC calibration curve.

NOTE   This concentration is often chosen to be around 80 % of the upper limit of the measuring range or around the emission limit value.

If the repeatability standard deviation at span point is determined during the lack of fit test, the highest value of reference gas (span point) applied during the test shall be used.

The measured values at the span point shall be determined by application of the reference gas and recording 20 consecutive individual injections. The measured signals obtained shall be used to determine the repeatability standard deviation at span point using Equation (B.3).

The repeatability standard deviation at span point shall meet the performance criterion specified in Table 2.

B.5 Sampling system and leakage check

A check of the sampling system shall be carried out before each measurement series. This includes the leak test.

The entire sampling system shall be checked by supplying repeatedly zero gas and test gas directly at the sampling probe. The test gas should have a methane concentration of about 80 % of the selected measuring range. Small deviations shall be corrected. Large deviations indicate malfunctions. The causes shall be identified and eliminated. Then the sampling system shall be checked again.

Annex C
(informative)

Typical performance characteristics

C.1 General

To determine performance characteristics, a round robin test was carried out which included three comparison tests, where five testing laboratories determined methane in gas samples from different sources after each change of GC conditions:

— test gases from gas cylinders;

— test gases which were provided via a test gas manifold in a ring test laboratory;

— real waste gas (gas engine of a sewage treatment plant).

The evaluation of the data is based on ISO 5725-2[1].

C.2 Measurement uncertainty

C.2.1 Comparison measurements using gas cylinders

The repeatability standard deviation at standard conditions (0 °C, 1 013 hPa) ranged from 0,057 mg/m^3 to 1,02 mg/m^3 (1,2 % to 1,6 %), the reproducibility standard deviation from 0,26 mg/m^3 to 4,58 mg/m^3 (7,1 % to 7,9 %). The relative standard uncertainty is calculated to range from 9,4 % to 10,8 % (see Table C.1).

Table C.1 — Standard uncertainty calculated from the results of the comparison measurements using test gases from gas cylinders with five testing laboratories participating

Parameter	Gas cylinder test		
	1	2	3
Number of analyses	14	14	14
Grand mean (0 °C, 1 013 hPa), mg/m^3	3,8	30,6	60,0
Standard uncertainty (0 °C, 1 013 hPa), mg/m^3	0,36	3,31	5,73
Relative standard uncertainty (standard uncertainty divided by the grand mean), %	9,4	10,8	9,6

C.2.2 Comparison measurements using a test gas manifold

The results of the comparison measurements using a test gas manifold were comparable with respect to repeatability standard deviation and reproducibility standard deviation from the gas cylinder test when only CH_4 was included as test component in the test gas. The relative standard uncertainty is in the range between 1 % and 16 % (see Table C.2).

Table C.2 — Standard uncertainty calculated from the results of the comparison measurements at the test gas manifold with five testing laboratories participating

Parameter	Gas manifold test				
	1	2	3	4	5
Number of participants	5	4	4	3	5
Number of analyses	10	8	8	6	10
Grand mean (0 °C, 1 013 hPa), mg/m^3	8,28	62,5	33,	23,9	14,5
Standard uncertainty (0 °C, 1 013 hPa), mg/m^3	1,33	0,23	0,44	2,05	0,99
Relative standard uncertainty (standard uncertainty divided by the grand mean), %	16,2	0,4	1,3	8,6	6,8

When interfering components (CO_2, CO, NO_2, SO_2, and C_3H_8) were added to the test gas mixtures, the relative standard uncertainty was in the range from 4 % to 10 %, i.e. no significant deviation was observed.

C.2.3 Comparison measurements using real waste gases

The results for the standard uncertainty of the comparison measurements with the waste gas of a gas engine of a sewage treatment plant were increased compared to the results at the test gas manifold. The relative standard uncertainties are in the range between 3 % and 15 % (see Table C.3).

Table C.3 — Standard uncertainty calculated from the results of the comparison measurements at the gas engine of a waste water purification plant with five testing laboratories participating

Parameter	Real waste gas test									
	1	2	3	4	5	6	7	8	9	10
Number of participants	5	6	6	6	6	5	6	6	6	3
Number of analyses	5	6	6	6	6	5	6	6	6	3
Grand mean (0 °C, 1 013 hPa), mg/m^3	446,1	302,9	129,8	81,5	38,5	60,4	93,0	242,4	500,6	1374,9
Standard uncertainty (0 °C, 1 013 hPa), mg/m^3	55,4	21,9	6,45	2,65	1,69	3,50	9,30	27,4	34,6	204,6
Relative standard uncertainty (standard uncertainty divided by the grand mean), %	12,4	7,2	5,0	3,2	4,4	5,8	10,0	11,3	6,9	14,9

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