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Stationary source emissions — Automatic method for the determination of the methane concentration using flame ionisation detection (FID)

Émissions de sources fixes — Méthode automatique pour la détermination de la concentration en méthane par détection à ionisation de flamme (FID)

Reference number
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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 25140 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 and anthropogenic sources. 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 — Automatic method for the determination of the methane concentration using flame ionisation detection (FID)

1 Scope

This International Standard specifies the principle, the essential performance criteria, and quality assurance and quality control procedures for an automatic method for measuring methane in the waste gas of stationary sources using flame ionisation detection. It is applicable to measurements of methane in dry or wet waste gases. The method allows continuous monitoring with permanently installed measuring systems as well as intermittent measurements of methane emissions.

NOTE 1 This International Standard is specific to automatic methods for measuring methane in the waste gas of stationary sources using flame ionisation detection. It supplements the general requirements of other international or national standards on performance testing, QA/QC procedures, and the test report as specified, for example, in EN 15267-3[7], EN 14181[5], and EN 15259[6].

This International Standard does not specify an independent method of measurement.

NOTE 2 An independent method of measurement, e.g. to calibrate or validate permanently installed measuring systems, is specified in ISO 25139[3].

NOTE 3 In EN 14181[5], “independent method of measurement” is called “standard reference method (SRM)”.

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 9169:2006, *Air quality — Definition and determination of performance characteristics of an automatic measuring system*

ISO 14956, *Air quality — Evaluation of the suitability of a measurement procedure by comparison with a required measurement uncertainty*

ISO 20988, *Air quality — Guidelines to estimating measurement uncertainty*

3 Terms and definitions

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

3.1
automatic measuring system
AMS
⟨air quality⟩ measuring system interacting with the waste gas under investigation, returning an output signal proportional to the physical unit of the measurand in unattended operation

NOTE 1 Adapted from ISO 9169:2006, 2.1.2.

NOTE 2 In the sense of this document, an AMS is a system that can be attached to a duct to continuously or intermittently measure and record the mass concentrations of methane passing through the duct.

3.2
analyser

⟨stationary source emissions⟩ analytical part in an extractive or *in situ* automatic measuring system

NOTE Adapted from ISO 12039:2001[2], 3.3.

3.3
measurand

particular quantity subject to measurement

[ISO/IEC Guide 98-3:2008[4], B.2.9]

EXAMPLE The mass concentration of methane in air.

3.4
mass concentration

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

[ISO 12039:2001[2], 3.10]

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

3.5
independent reading

⟨stationary source emissions⟩ reading that is not influenced by a previous individual reading by separating two individual readings by at least four response times

3.6
individual reading

⟨stationary source emissions⟩ reading averaged over a time period equal to the response time of the automatic measuring system

3.7
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]

3.8
adjustment

⟨automatic measuring system⟩ operation of bringing an automatic measuring system into a state of performance suitable for its use

NOTE Adjustment can be automatic, semi-automatic or manual.

[ISO 9169:2006, 2.1.5]

3.9
calibration

⟨stationary source emissions⟩ procedure for establishing the statistical relationship between values of the measurand indicated by the automatic measuring system and the corresponding values given by an independent method of measurement implemented simultaneously at the same measuring point

NOTE 1 An independent method of measurement for the purpose of calibration of permanently installed methane measuring systems is specified in ISO 25139[3].

NOTE 2 In EN 14181[5], “independent method of measurement” is called “standard reference method (SRM)”.

3.10
interference
⟨air quality⟩ negative or positive effect upon the response of the measuring system, due to a component of the sample that is not the measurand

3.11
zero gas
⟨stationary source emissions⟩ gas or gas mixture used to establish the zero point on a calibration curve within a given concentration range

[ISO 12039:2001[2], 3.4.2]

3.12
span gas
gas or gas mixture used to adjust and check a specific point on a calibration curve

NOTE Adapted from ISO 12039:2001[2], 3.4.1.

3.13
reference gas
⟨stationary source emissions⟩ gas of known, reliable and stable composition that may be used to check the response of an automatic measuring system and to calibrate the automatic measuring system

3.14
zero point
⟨stationary source emissions⟩ specified value of the output quantity (measured signal) of the automatic measuring system and which, in the absence of the measured component, represents the zero crossing of the calibration line

3.15
span point
value of the output quantity (measured signal) of the automatic measuring system for the purpose of calibration or adjustment that represents a correct measured value generated by a reference material

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

3.16
performance characteristic
⟨air quality⟩ one of the quantities assigned to equipment in order to define its performance

NOTE Performance characteristics can be described by values, tolerances or ranges.

3.17
response time
⟨air quality⟩ time interval between the instant when a stimulus is subjected to a specified abrupt change and the instant when the response reaches and remains within specified limits around its final stable value, determined as the sum of the lag time and the rise time in the rising mode, and the sum of the lag time and the fall time in the falling mode

[ISO 9169:2006, 2.2.4]

3.18
lag time

⟨air quality⟩ by convention, time taken for the output signal to reach 10 % of the final change in the output signal when a step function is applied by applying a reference material to the automatic measuring system initially in the basic state

[ISO 9169:2006, 2.2.2]

3.19
rise time

⟨air quality⟩ by convention, time taken for the output signal to pass from 10 % to 90 % of the final change in the output signal when a reference material is abruptly applied to the automatic measuring system initially in the basic state

NOTE For instruments where transient oscillations occur in the approach to the final output signal, 90 % of the final change is considered as reached when the oscillations fall to less than 10 % of the final change in the output signal.

[ISO 9169:2006, 2.2.3]

3.20
fall time

⟨air quality⟩ by convention, time taken for the output signal to pass from 90 % to 10 % of the initial output signal produced by a reference material applied to the automatic measuring system, when the application of this reference material is abruptly terminated to put the automatic measuring system in the basic state

NOTE For instruments where transient oscillations occur in the approach to the final output signal, the 10 % of the initial output signal is considered as reached when the oscillations in the vicinity of the final output signal fall to less than 10 % of the initial output signal.

[ISO 9169:2006, 2.2.1]

3.21
linearity

⟨air quality⟩ maximum deviation between a linear calibration curve and the true value of the measurand, evaluated in practice as the maximum lack of fit within the measuring range

[ISO 9169:2006, 2.1.20]

3.22
lack of fit

systematic deviation, within the range of application, between the accepted value of a reference material applied to the measuring system and the corresponding result of measurement produced by the measuring system

[ISO 9169:2006, 2.2.9]

3.23
residence time

⟨stationary source emissions⟩ time period for the sampled gas to be transported from the inlet of the probe to the inlet of the measurement cell

3.24
period of unattended operation

maximum interval of time for which the performance characteristics remain within a predefined range without external servicing, e.g. refill, adjustment

[ISO 9169:2006, 2.2.11]

NOTE The period of unattended operation is often called maintenance interval.

3.25
uncertainty (of measurement)
measurement uncertainty
parameter associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand

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

3.26
standard uncertainty
uncertainty of the result of a measurement expressed as a standard deviation

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

3.27
expanded uncertainty
quantity defining an interval about the result of a measurement that may be expected to encompass a large fraction of the distribution of values that could reasonably be attributed to the measurand

NOTE 1 The fraction may be viewed as the coverage probability or level of confidence of the interval.

NOTE 2 To associate a specific level of confidence with the interval defined by the expanded uncertainty requires explicit or implicit assumptions regarding the probability distribution characterized by the measurement result and its combined standard uncertainty. The level of confidence that may be attributed to this interval can be known only to the extent to which such assumptions may be justified.

NOTE 3 Expanded uncertainty is termed overall uncertainty in paragraph 5 of Recommendation INC-1 (1980).

[ISO/IEC Guide 98-3:2008[4], 2.3.5 and 0.7 for a translation of Recommendation INC-1 (1980)]

4 Symbols and abbreviated terms

AMS	automatic measuring system
e_i	residual (lack of fit) at level i
FID	flame ionisation detection; flame ionisation detector
i	series element number
$M_{\mathrm{CH_4}}$	molecular mass of methane (16 g/mol)
$M_{\mathrm{H_2O}}$	molecular mass of water (18 g/mol)
$m_{\mathrm{H_2O,\,v}}$	mass of water vapour
n	number of measurements
n_{neg}	number of interfering substances with a negative effect on the measured signal
n_{pos}	number of interfering substances with a positive effect on the measured signal
QA/QC	quality assurance and quality control
s_r	repeatability standard deviation
S_{pos}	sum of the positive interfering effects
S_{neg}	sum of the negative interfering effects

V_0	volume of the dry gas sampled
V_m	standard molar volume (22,4 l/mol)
$\overline{x}$	average of the measured values x_i
x_i	ith measured value
$\overline{x}_i$	average of the measured values at level i
$\hat{x}_i$	value estimated by the regression line at level i
$x_{i,\ \mathrm{neg}}$	ith negative deviation in units of the measurand (e.g. mass concentration) caused by an interfering substance with a negative effect on the measured signal
$x_{i,\ \mathrm{pos}}$	ith positive deviation in units of the measurand (e.g. mass concentration) caused by an interfering substance with a positive effect on the measured signal
$\gamma_{\mathrm{CH_4,\ s}}$	methane mass concentration at standard conditions of temperature and pressure (wet gas)
$\gamma_{\mathrm{CH_4,\ (H_2O)_0}}$	methane mass concentration at reference conditions of water vapour (dry gas)
$\gamma_{\mathrm{CH_4,\ O_2}}$	methane mass concentration at reference conditions of oxygen
γ_i	test gas concentration at level i
$\rho_{\mathrm{H_2O,\ v}}$	density of water vapour
$\varphi_{\mathrm{CH_4,\ o}}$	methane content, as a volume fraction, at operating conditions
$\varphi_{\mathrm{H_2O,\ m}}$	measured water vapour content, as a volume fraction, in the waste gas
$\varphi_{\mathrm{O_2,\ m}}$	measured oxygen content, as a volume fraction, in the waste gas
$\varphi_{\mathrm{O_2,\ ref}}$	reference oxygen content, as a volume fraction

5 Apparatus and principles of operation

5.1 Measurement method

5.1.1 Analyser. The extractive analytical system consists of two elements: the flame ionisation detector (FID) and the associated sampling system.

Measurement by FID is based on the ionisation of organically bound carbon atoms in a hydrogen flame. The ionisation current measured by the FID depends on the number of carbon-hydrogen bonds in the organic compounds broken during combustion in the fuel gas flame, the nature of bonding (straight chain or branched chain) and whether other bound elements are present.

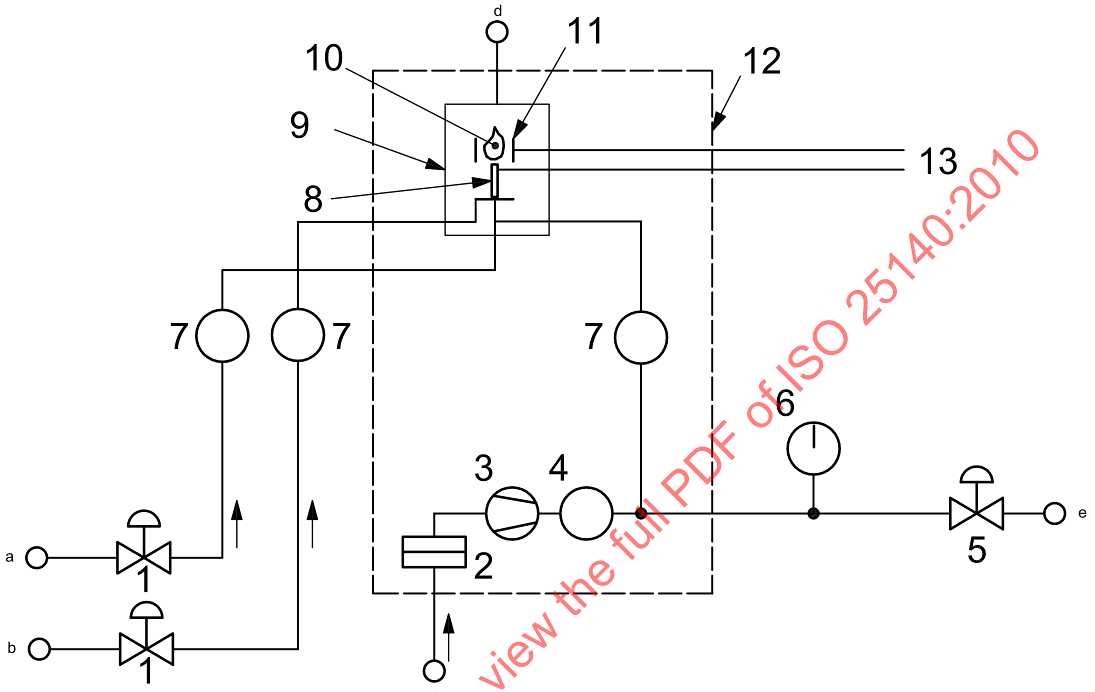
The main advantage of the FID is that it responds strongly to organic compounds and less to inorganic waste gas components, such as CO, CO_2, NO, and H_2O.

To determine methane alone, the FID is equipped with a catalytic converter, which oxidises all organic compounds in the sample gas except methane. Care shall be taken to avoid poisoning or contamination of the converter by sulfur-, nitrogen-, and chlorine-containing compounds. To avoid memory effects (signal offsets caused by contamination of the tube system within the instrument) and response delays in the system, the catalytic converter should be located close to the FID and heated.

NOTE 1 The catalytic converter usually consists of a heatable stainless steel tube filled with catalytic material.

NOTE 2 Various manufacturers produce specific “methane FID” instruments with an integrated converter.

Figure 1 is a schematic diagram showing the principle of operation of the FID.



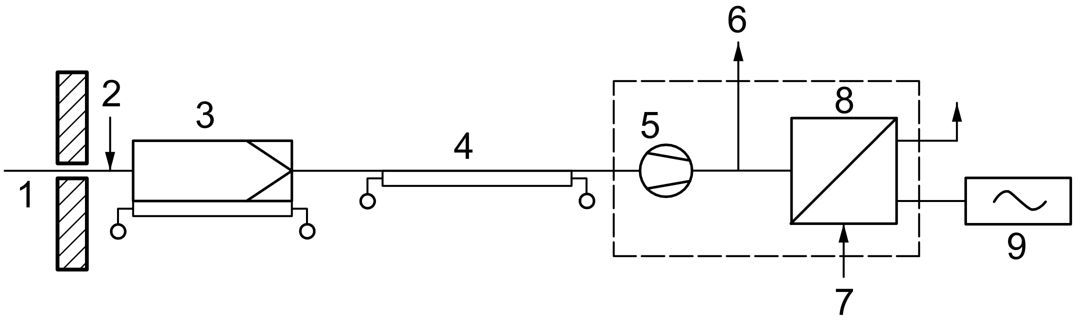
Key

1	pressure regulator	11	electrode
2	fine dust filter	12	heated housing
3	sampling gas pump	13	DC voltage
4	converter	a	Fuel gas.
5	back-pressure regulator	b	Combustion air.
6	pressure gauge	c	Sample gas.
7	flow meters	d	Gas outlet.
8	nozzle	e	Bypass.
9	combustion chamber		
10	flame		

Figure 1 — Schematic diagram of the principle of operation of the FID

5.1.2 Sampling system. Sampling is the process of extracting a small portion which is truly representative of the composition of the main gas stream from a large quantity of waste gas.

A partial flow of the waste gas is directly fed into the FID analyser containing the catalytic converter via the sampling probe, the particle filter and the heated sampling line. An example of the set-up of the measuring system is shown in Figure 2. The sampling device, including the filter needed to remove fine particles, which could clog the burner, is heated to avoid sample condensation.



Key

1	sampling probe, heated (if necessary)	6	bypass (optional)
2	zero and span gas inlet	7	test gas inlet for functional tests
3	particle filter (in-stack or out-stack), heated	8	FID including catalytic converter
4	sampling line, heated	9	data evaluation system
5	external sample pump (optional), heated		

Figure 2 — Schematic diagram of the measuring system set-up

The sampling device shall:

a) be made of a material that is chemically and physically inert to the constituents of the waste gas under analysis;

NOTE Stainless steel, perfluoroalkoxy, polytetrafluoroethylene and polypropylenefluoride are well-proven construction materials.

b) be designed to ensure a sample residence time less than 60 s (with long sampling lines or high flow resistance, the use of an external pump with bypass is recommended);

c) be heated throughout, and where measurements are taken in hot gases, the temperature of the coolest point shall be at least 20 °C above the waste gas temperature to avoid condensation of water vapour or other components of the waste gas, and should not exceed 200 °C;

d) have a heated filtering device upstream of the sampling line to trap all particles liable to impair the operation of the apparatus;

e) have an inlet for applying zero and span gases at or close to the entry nozzle of the sampling probe, upstream of the filter.

5.1.3 Data display and recording. The FID analyser shall have an output signal with a live zero and be able to show negative values.

Automatic measuring systems (AMSs) for intermittent monitoring should have a means of averaging the continuous output signal of the FID over a stated reference time period (e.g. 30 min). The averaged output signal should then be converted to measured values in units of the measurand (mass concentration) by use of the calibration function. Where required, a means of converting the measured values to reference conditions of water vapour and oxygen content shall be available. The AMS should be capable of displaying and recording the measured methane mass concentrations.

For permanently installed AMS for continuous monitoring, the plant electronic data evaluation system can be used for the calculation of the measured values at operating conditions, the conversion to reference conditions and for displaying and recording of the measured methane concentrations.

NOTE The data display can be a separate device.

5.2 Performance criteria fulfilment

5.2.1 General.

The FID shall comply with the performance criteria specified in Table 1. These performance criteria are determined as specified in 5.2.2 to 5.2.4.

5.2.2 General performance test.

The manufacturer of the AMS shall demonstrate in a general performance test that the relevant performance criteria listed in Table 1 are fulfilled by the instrument type. The test procedures of this general performance test shall comply with relevant international or national standards.

5.2.3 Ongoing quality assurance and quality control (QA/QC) in the laboratory.

The user of the AMS shall demonstrate during regular laboratory tests conducted within the ongoing QC programme that the relevant performance criteria listed in Table 1 are fulfilled for the specific AMS.

5.2.4 Quality assurance during operation in the field.

The user of the AMS has to check during field operation that the relevant performance criteria listed in Table 1 are fulfilled.

6 Performance criteria and determination of the performance characteristics

6.1 Performance criteria

Table 1 specifies the performance criteria of the analyser and the measuring system to be evaluated at three levels: during general performance test; by means of ongoing QA/QC in the laboratory; and during field operation.

Table 1 — Relevant performance criteria of the analyser and the measuring system to be evaluated during the general performance test and by means of ongoing QA/QC in the laboratory and during field operation

Performance characteristic	Performance criterion	General performance test	QA/QC in the laboratory	Field application
Response time	⩽ 60 s	×	×	×[f]
Repeatability standard deviation at zero point	⩽ 1,0 % of upper limit of the lowest measuring range used[a]	×	×	—
Repeatability standard deviation at span point	⩽ 2,0 % of upper limit of the lowest measuring range used[a]	×	×	—
Lack of fit	⩽ 2,0 % of upper limit of the lowest measuring range used[a]	×	×	—
Influence of atmospheric pressure[b], for a pressure change of ± 2 kPa	⩽ 1,0 % of upper limit of the lowest measuring range used[a]	×	—	—
Influence of sample volume flow	⩽ 2,0 % of upper limit of the lowest measuring range used[a]	×	—	—
Influence of sample gas pressure at span point, for a pressure change of 3 kPa	⩽ 2,0 % of upper limit of the lowest measuring range used[a]	×	—	—
Influence of ambient temperature, for a change of 10 °C	⩽ 2,0 % of upper limit of the lowest measuring range used[a]	×	—	—

Table 1 (*continued*)

Performance characteristic	Performance criterion	General performance test	QA/QC in the laboratory	Field application
Influence of voltage, at −15 % below and at +10 % above nominal supply voltage	⩽ 2,0 % of upper limit of the lowest measuring range used[a]	×	—	—
Influence of inorganic interference gases[c]	⩽ 4,0 % of upper limit of the lowest measuring range used[a]	×	×	—
Oxygen interference	⩽ 2,0 % of upper limit of the lowest measuring range used[a]	×	×	—
Converter efficiency, tested with ethane	⩾ 98,0 %	×	×	—
Methane loss[d]	⩽ 15,0 %	×	—	—
Zero drift[e], within 24 h	⩽ 2,0 % of upper limit of the lowest measuring range used[a]	×	—	×
Span drift[e], within 24 h	⩽ 2,0 % of upper limit of the lowest measuring range used[a]	×	—	×
Period of unattended operation for permanently installed AMS	⩾ 8 days	×	—	×
Losses and leakage in the sampling line and conditioning system	⩽ 2,0 % of upper limit of the lowest measuring range used[a]	—	—	×

[a] The upper limit of the lowest measuring range used should be selected depending on the application such that the measured values lie within 20 % to 80 % of the analyser range.

[b] The tested sample pressure is defined in the manufacturer's recommendations.

[c] See Table B.1.

[d] The temperature dependent methane loss is compensated for in the calibration process.

[e] The frequency of zero and span checks is specified in Table 2.

[f] If sampling line length exceeds the length applied in the general performance test.

6.2 Determination of the performance characteristics and measurement uncertainty

6.2.1 Performance test

The performance characteristics of the AMS shall be determined during the general performance test in accordance with applicable international or national standards. The values of the performance characteristics determined shall meet the performance criteria specified in Table 1.

NOTE Performance tests for automatic emission measuring systems are specified e.g. in ISO 9169 and EN 15267-3[7].

The ambient conditions applied during the general performance test shall be documented.

The overall uncertainty of the AMS measured values shall be calculated in accordance with ISO 14956 on the basis of the performance characteristics determined during the general performance test and shall meet the uncertainty specified for the measurement objective.

6.2.2 Ongoing quality control

The user shall check specific performance characteristics during ongoing operation of the measuring system with a periodicity specified in Table 2. The procedures for the determination of these performance characteristics are described in Annex B. Procedures for instruments for intermittent measurements differ from those for permanently installed AMS for continuous monitoring at plants.

The measurement uncertainty during field application shall be determined by the user of the measuring system in accordance with applicable international or national standards. The uncertainty of the measured values under field operation is not only influenced by the performance characteristics of the analyser itself but also by uncertainty contributions due to:

a) the sampling line and conditioning system;

b) the site specific conditions;

c) the calibration gases used.

7 Measurement procedure

7.1 General

The AMS shall be operated according to the manufacturer's instructions.

The QA/QC procedures specified in Clause 8 shall be strictly observed.

During the measurement, the ambient conditions should be in the ranges applied during the general performance test.

7.2 Choice of the measuring system

It shall be checked that the chosen analyser is appropriate for the measurement task.

To choose an appropriate analyser, sampling line and conditioning system, the following characteristics should be known before the field operation:

a) ambient temperature range;

b) temperature of the waste gas;

c) water vapour content of the waste gas;

d) dust load of the waste gas;

e) expected concentration range of methane;

f) expected concentration of potentially interfering substances, including at least those listed in Table B.1.

To avoid long response times and memory effects, the sampling line should be as short as possible. If necessary, a bypass pump should be used. An appropriate heated filter shall be used.

Before conducting field measurements, the user shall verify that the necessary QA/QC procedures have been performed.

7.3 Sampling location

It is necessary to ensure that the gas concentrations measured are representative of the average conditions inside the waste gas duct. The measurement site, the measurement section and the sampling points shall be selected in accordance with applicable international or national standards.

NOTE The selection of the measurement site, the measurement section and the sampling points are described, for example, in EN 15259[6].

In addition, the sampling location shall be chosen with regard to safety of personnel.

7.4 Data collection

The calibrated FID measured values at operating conditions of the waste gas shall be recorded by an internal or external data logging system and averaged in accordance with the measurement task.

The volume content of water vapour and oxygen (if necessary) in the waste gas shall also be measured in parallel and averaged over the sampling period of the methane measurement to express the methane concentration for dry waste gas conditions and, if required, oxygen reference conditions.

7.5 Calculation

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

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

$$\gamma_{CH_4,\,s} = \varphi_{CH_4,\,o} \cdot \frac{M_{CH_4}}{V_m} \qquad (1)$$

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 mass concentration, $\gamma_{CH_4,s}$, shall be corrected to the methane mass concentration at reference conditions of water vapour (dry gas), $\gamma_{CH_4,(H_2O)_0}$, using Equation (2):

$$\gamma_{CH_4,(H_2O)_0} = \gamma_{CH_4,\,s}\left(\frac{100\ \%}{100\ \% - \varphi_{H_2O,\,m}}\right) \qquad (2)$$

where

$\gamma_{CH_4,s}$ is the methane mass concentration in the wet gas at reference conditions of temperature and pressure;

$\varphi_{H_2O,\,m}$ is the measured 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 a mass concentration, Equation (3) shall be used to calculate the water vapour content, as a volume fraction, φ_{H_2O}, in the waste gas:

$$\varphi_{H_2O} = \frac{m_{H_2O,\,v}/\rho_{H_2O,\,v}}{(m_{H_2O,\,v}/\rho_{H_2O,\,v}) + V_0} \qquad (3)$$

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 mass concentration at standard conditions of temperature and pressure, $\gamma_{\mathrm{CH_4,\,s}}$, shall be corrected to reference conditions of oxygen, designated $\gamma_{\mathrm{CH_4,\,O_2}}$, using Equation (4):

$$\gamma_{\mathrm{CH_4,O_2}} = \gamma_{\mathrm{CH_4,\,s}} \left(\frac{21\,\% - \varphi_{\mathrm{O_2,\,ref}}}{21\,\% - \varphi_{\mathrm{O_2,\,m}}} \right) \qquad (4)$$

where

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

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

8 Quality assurance and quality control procedures

8.1 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.

The following applications of the automatic measuring system have to be distinguished:

a) AMS for intermittent measurements (8.3);

b) permanently installed AMS for continuous monitoring (8.4).

8.2 Frequency of checks

Table 2 shows the minimum required 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 QA/QC during the operation

Check	Minimum frequency	
	AMS for intermittent measurements	**Permanently installed AMS**
Response time	once a year	once a year
Repeatability standard deviation at zero point	once a year	once a year
Repeatability standard deviation at span point	once a year	once a year
Lack of fit	once a year and after repair of the AMS	once a year and after repair of the AMS
Calibration	—	at regular time intervals specified, for example, in legislation or applicable standards by comparison with an independent method of measurement
Interference check	once a year	once a year
Converter check	once for each measurement series	once a year
Sampling system and leakage check	once for each measurement series	once a year

Table 2 (*continued*)

Check	Minimum frequency	
	AMS for intermittent measurements	**Permanently installed AMS**
Cleaning or changing of particulate filters[a] at the sampling inlet and at the monitor inlet	once for each measurement series, if needed	once in the period of unattended operation
Zero drift	every 3 h and at the end of measuring period	once in the period of unattended operation
Span drift	every 3 h and at the end of measuring period	once in the period of unattended operation
Regular maintenance of the analyser	as required by the manufacturer	once in the period of unattended operation

[a] The particulate filter shall be changed periodically depending on the dust load at the sampling site. During this filter change, the filter housing shall be cleaned.

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

8.3 AMS for intermittent measurements

8.3.1 General

AMS for intermittent measurements shall be adjusted and checked in accordance with 8.3.2 at frequencies specified in Table 2.

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

8.3.2 Adjustments and functional tests

8.3.2.1 Instrument adjustment

Instrument adjustments with zero and span gases shall be carried out at least at the beginning of each measurement series. The safety procedures detailed in Annex C shall be followed.

The zero and span gas shall be introduced under the same flow and pressure conditions using the sample port of the instrument or according to the manufacturer's instructions when using individual zero and span ports. The adjustment procedure shall be carried out as follows:

a) feed zero gas into the FID and set the zero;

b) feed span gas and adjust the instrument accordingly;

c) feed zero gas into the FID once more and check that the reading returns to zero.

Steps a) to c) have to be repeated, if the reading does not return to zero.

8.3.2.2 Response time

The response time of the AMS response shall be checked in accordance with B.2 at least once a year. It shall be checked in the field application if the sampling line length exceeds the length applied in the general performance test.

8.3.2.3 Repeatability standard deviation at zero point

The repeatability standard deviation at zero point shall be checked in accordance with B.3 at least once a year.

8.3.2.4 Repeatability standard deviation at span point

The repeatability standard deviation at span point shall be checked in accordance with B.4 at least once a year.

8.3.2.5 Linearity check

The linearity of the AMS response shall be checked in accordance with B.5 at least once a year.

8.3.2.6 Interference check

The interference shall be checked in accordance with B.6 at least once a year.

8.3.2.7 Check of the converter efficiency

The converter efficiency shall be checked in accordance with B.7 at least once for each measurement series.

8.3.2.8 Sampling system and leakage check

The sampling system of the AMS shall be checked in accordance with B.8 at least once for each measurement series.

8.3.2.9 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.

8.3.2.10 Zero and span drift

The zero and span drift shall be checked in accordance with B.9 at least every 3 h and at the end of the measuring period.

8.3.2.11 Regular maintenance of the analyser

The regular maintenance of the analyser shall be performed as required by the manufacturer.

8.3.2.12 Measurement uncertainty

The uncertainty of measured values obtained by AMS for intermittent monitoring shall be determined in accordance with the principles laid down in ISO 20988. The measurement uncertainty shall be representative of the intended application of the AMS. It shall take into account all relevant sources of uncertainty.

NOTE The uncertainty of measured values obtained by AMS for intermittent monitoring can be determined by a direct or by an indirect approach described in ISO 20988. The direct approach can be based on comparison measurements with an independent method of measurement under conditions of the intended operation of the AMS. ISO 20988 describes procedures to evaluate such comparison measurements. A detailed description of the indirect approach is given in ISO 14956.

The uncertainty of the measured values shall meet the uncertainty criterion specified for the measurement objective.

8.4 Permanently installed AMS

8.4.1 General

Permanently installed AMS for continuous monitoring shall meet the performance criteria specified in Table 1.

General QA/QC procedures for permanently installed AMS specified in national or international standards shall be observed.

NOTE General QA/QC procedures for permanently installed AMS are specified, for example, in EN 14181[5].

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

8.4.2 Adjustments and functional tests

8.4.2.1 Instrument adjustment

Permanently installed AMS shall be adjusted in accordance with 8.3.2.1 at least once in the period of unattended operation.

8.4.2.2 Response time

The response time of the AMS response shall be checked in accordance with B.2 at least once a year.

8.4.2.3 Repeatability standard deviation at zero point

The repeatability standard deviation at zero point shall be checked in accordance with B.3 at least once a year.

8.4.2.4 Repeatability standard deviation at span point

The repeatability standard deviation at span point shall be checked in accordance with B.4 at least once a year.

8.4.2.5 Linearity check

The linearity of the AMS response shall be checked in accordance with B.5 at least once a year.

8.4.2.6 Interference check

The interference shall be checked in accordance with B.6 at least once a year.

8.4.2.7 Check of the converter efficiency

The converter efficiency shall be checked in accordance with B.7 at least once a year.

8.4.2.8 Sampling system and leakage check

The sampling system of the AMS shall be checked in accordance with B.8 at least once a year.

8.4.2.9 Cleaning or changing of particulate filters

The particulate filter shall be changed at least once in the period of unattended operation. During the filter change the filter housing shall be cleaned.

8.4.2.10 Zero and span drift

The zero and span drift shall be checked in accordance with B.9 at least once in the period of unattended operation. This manual check is also needed for AMS with internal automatic zero and span checks.

8.4.2.11 Regular maintenance of the analyser

The regular maintenance of the analyser shall be performed once in the period of unattended operation.

8.4.3 Calibration, validation, and measurement uncertainty

Permanently installed AMS for continuous monitoring shall be calibrated and validated by comparison with an independent method of measurement. The validation shall include the determination of the uncertainty of the measured values obtained by the calibrated AMS.

NOTE 1 The manual gas chromatographic method for the determination of methane specified in ISO 25139[3] can be used as an independent method of measurement.

The AMS shall be subject to adjustments and functional tests according to 8.4.2 before each calibration and validation.

The calibration and validation of the AMS shall be performed at regular intervals and after repair of the analyser in accordance with applicable national or international standards.

The uncertainty of measured values obtained by permanently installed AMS for continuous monitoring shall be determined by comparison measurements with an independent method of measurement as part of the calibration and validation of the AMS. This ensures that the measurement uncertainty is representative of the application at the specific plant.

NOTE 2 The determination of the uncertainty of measured values obtained by permanently installed AMS for continuous monitoring on the basis of a comparison with an independent method of measurement is described, for example, in ISO 20988 and EN 14181[5].

The uncertainty of the measured values shall meet the uncertainty criterion specified for the measurement objective.

9 Test report

The test report shall be in accordance with international or national regulations. If not specified otherwise, it shall include at least the following information:

a) reference to this International Standard (ISO 25140:2010);

b) description of the measurement objective;

c) principle of gas sampling;

d) information about the analyser and description of the sampling line and conditioning system;

e) identification of the analyser used, and analyser’s performance characteristics as listed in Table 1;

f) operating range;

g) details of the quality and the concentration of the span gases used;

h) description of plant and process;

i) identification of the sampling plane;

j) actions taken to achieve representative samples;

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

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

m) changes in the plant operations during sampling;

n) sampling date, time and duration;

o) time averaging on relevant periods;

p) measured values;

q) measurement uncertainty;

r) results of any checks;

s) any deviations from the requirements of this International Standard.

NOTE Requirements for the test report are specified e.g. in EN 15267-3[7] for the results of performance tests, in EN 15259[6] for the results of intermittent monitoring, and in EN 14181[5] for the results of continuous monitoring.

Annex A
(normative)

Operational gases

A.1 General

A number of operational gases are required when using this International Standard.

A.2 Combustion air

The combustion air shall consist of synthetic (hydrocarbon-free) or purified air. The hydrocarbon volume fraction should not exceed 2,0 % of the upper limit of the measuring range used during the whole operation.

A.3 Fuel gas

The fuel gas for the FID usually consists of hydrogen. If required by the FID manufacturer, the fuel gas can be a hydrogen-helium mixture or a hydrogen-nitrogen mixture.

The purity of the fuel gas used shall be at least 99,999 %.

For safety reasons the fuel gas line should be made of metal.

A.4 Zero gas

The zero gas shall consist of hydrocarbon-free synthetic air. The hydrocarbon volume fraction should not exceed 1,0 % of the upper limit of the measuring range used.

NOTE Combustion air can be suitable if it is sufficiently purified.

A.5 Span gas

Span gas shall consist of methane in synthetic air. It shall have a known concentration with a maximum permissible expanded uncertainty of 2,0 % of its nominal value traceable to applicable standards.

The span gas concentration should be about 70 % of the upper limit of the selected measuring range.

A.6 Reference gas

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

The reference gas concentration should be about 70 % of the upper limit of the selected measuring range.

A.7 Test gas for checking the converter efficiency

Test gas for checking the converter efficiency shall consist of ethane in synthetic air. The concentration shall be in the range of the methane concentration expected.

Annex B
(normative)

Determination of the performance characteristics of an FID to be applied in the ongoing quality control (QA/QC) procedures

B.1 General

Before determining the performance characteristics of an FID, the instrument shall be set up according to the procedure detailed in 8.3.2.

B.2 Response time

The response time shall be determined by applying a step change between zero gas and span gas of about 70 % of the upper limit of the lowest measuring range used. The zero and test gas shall be applied to the FID at the sample gas inlet.

The response time is the time interval between the instant of the step change and the instant when the response reaches and remains within 10 % of the step change around the final stable value. It is determined as the sum of the lag time and the rise time in the rising mode, and the sum of the lag time and the fall time in the falling mode.

The step change produced by the test facility shall have a rise time (between 10 % and 90 % of the step change) less than 10 % of the averaging time to be applied during the tests. If rise time and fall time differ, the longer one is to be taken for the computation of the response time.

For instruments where transient oscillations occur in the approach to the final output signal, the final output signal is considered as reached when the oscillations fall to within 10 % of the input step.

The response time shall be determined according to ISO 9169:2006, 6.3 by applying span gas at a level of about 70 % of the upper limit of the lowest measuring range used to the FID at the sample gas inlet.

B.3 Repeatability standard deviation at zero point

The repeatability standard deviation at zero point shall be determined by using a zero gas. First adjust the zero point of the FID. Then zero gas has to be applied at the zero and span gas inlet (see Figure 2).

If the repeatability standard deviation at zero point is determined during the lack of fit test, the reference material at zero concentration applied during the test shall be used.

The measured values of the AMS at zero point shall be determined after application of the reference material by waiting the time equivalent to one independent reading and then recording 20 consecutive individual readings.

The measured values obtained shall be used to determine the repeatability standard deviation, s_r, at zero point using Equation (B.1):

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

where

x_i is the ith measured value;

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

n is the number of measurements, n = 20.

The repeatability standard deviation at zero point shall meet the performance criterion specified in Table 1.

B.4 Repeatability standard deviation at span point

The repeatability standard deviation at span point shall be determined by application of a reference material at the span point (span gas).

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

The measured values of the AMS at span point shall be determined after application of the reference material by waiting the time equivalent to one independent reading and then recording 20 consecutive individual readings. The measured signals obtained shall be used to determine the repeatability standard deviation at span using Equation (B.1).

The repeatability standard deviation at span point shall meet the performance criterion specified in Table 1.

B.5 Lack of fit

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

The test gases shall be applied in an order, which avoids hysteresis effects.

Perform for each test gas with the concentration, γ_i, at least three consecutive measurements, each averaged over at least one response time. The residuals e_i (lack of fit) shall be determined on the basis of a linear regression as described in ISO 9169 or EN 15267-3[7]. In this test procedure, a regression line is established between the instrument readings of the FID (x values) and the test gas values (γ values). In the next step, the average $\overline{x}_i$ of FID readings at each test gas level is calculated. Then the deviation (residual) of the average to the corresponding value $\hat{x}_i$ estimated by the regression line is calculated according to Equation (B.2):

$$e_i = \left| \hat{x}_i - \overline{x}_i \right| \tag{B.2}$$

The deviations, e_i, at each test gas concentration shall meet the performance criterion specified in Table 1.

If the performance criterion is not met, the instrument response has to be corrected until the performance criterion is met.

B.6 Interference

B.6.1 General

The specific detection characteristics versus organic compounds depend, among other things, on the volume and the flow characteristics in the measurement chamber. If these characteristics vary then the overall sensitivity and the component-specific sensitivity (response factors) vary, too.

Oxygen (O_2) and carbon dioxide (CO_2) are considered the most significant interferents. In most analysers, these cross-sensitivities are minimised with internal techniques, so that their effect results in overestimations of the methane concentrations of less than 1,5 % for typical combustion process waste gases.

NOTE Specific investigations with respect to the oxygen cross-sensitivity within the round robin test described in Annex D indicated a maximum deviation of 2,3 %.

B.6.2 Determination of the effect of interfering substances except oxygen

Pass into the FID, hydrocarbon-free test gases containing various known concentrations of each interfering gas (see Table B.1). Note the measured values $x_{i,\text{ pos}}$ and $x_{i,\text{ neg}}$ expressed in units of the measurand.

Determine the effect of each interfering substance listed in Table B.1 separately.

Table B.1 — Interfering substances and default values to be used in the test

Interfering substance	Content
SO_2	250 mg/m^3
NO	800 mg/m^3
CO	400 mg/m^3
CO_2	18 % volume fraction
H_2O	25 % volume fraction
NOTE Complementary gas is nitrogen.	

Calculate the sums S_pos and S_neg of the positive and of the negative interfering effects of the mixture of substances, given in Table B.1 from the obtained individual effects $x_{i,\text{ pos}}$ and $x_{i,\text{ neg}}$ of the interfering substance using the Equation (B.3) and Equation (B.4):

$$S_\text{pos} = \sum_{i=1}^{n_\text{pos}} x_{i,\text{ pos}} \tag{B.3}$$

$$S_\text{neg} = \sum_{i=1}^{n_\text{neg}} x_{i,\text{ neg}} \tag{B.4}$$

where

$x_{i,\text{ pos}}$ is the positive deviation in units of the measurand (e.g. mass concentration) caused by an interfering substance with a positive effect on the measured signal;

$x_{i,\text{ neg}}$ is the negative deviation in units of the measurand (e.g. mass concentration) caused by an interfering substance with a negative effect on the measured signal;

n_{pos} is the number of interfering substances with a positive effect on the measured signal;

n_{neg} is the number of interfering substances with a negative effect on the measured signal.

The two values S_{pos} and S_{neg} shall comply with Table 1.

B.6.3 Determination of the effect of oxygen

Oxygen can affect both the zero point and the span value. To demonstrate the effect of oxygen, pass the following test gases into the FID:

a) zero gases:

   1) 100 % nitrogen,

   2) a mixture containing volume fractions of 90 % nitrogen and 10 % oxygen,

   3) a mixture containing volume fractions of 80 % nitrogen and 20 % oxygen;

b) span gases:

   1) a mixture containing volume fractions of 90 % nitrogen and 10 % oxygen with methane at 70 % of the upper limit of the lowest measuring range used,

   2) a mixture containing volume fractions of 80 % nitrogen and 20 % oxygen with methane at 70 % of the upper limit of the lowest measuring range used.

Calculate the interfering effect, S_{pos} and S_{neg}, of oxygen according to Equations (B.3) and (B.4). Both values shall comply with Table 1.

B.7 Converter efficiency

The converter efficiency shall be checked with ethane test gas with a concentration at about 70 % of the highest range used or at 50 mg/m^3, whichever is greater, which is fed into the analyser, and shall comply with Table 1. The response of the analyser is zero if the converter efficiency is 100 %.

NOTE 1 Some converter types require sufficient oxygen and water concentrations in the sampled gas in order to operate properly (see manufacturer's instructions).

The ethane breakthrough shall not exceed 2,0 % of the test gas concentration. If the ethane breakthrough exceeds the permissible value, the converter shall be checked and exchanged, if necessary.

A temperature-dependent methane loss can occur in the converter (see Figure B.1) during operation of the analyser. The methane loss need not be determined, as it is usually less than 15 % and is compensated for by the instrument or by the calibration.

Certain substances can affect the function of the catalytic converter adversely or even destroy the catalytic material. Critical substances are halogenated hydrocarbons, sulfur compounds, nitrogen oxides, ammonia and other organic and inorganic nitrogen compounds, silicones, plasticisers, metal vapour (e.g. mercury), and particulate matter (see Annex D). If those substances occur, the converter shall be regularly checked.

NOTE 2 Extremely high concentrations (> 5 000 mg/m^3) of organic substances (apart from methane) can overheat the converter and thus reduce drastically its efficiency.