
**Stationary source emissions —
Determination of total volatile organic
compounds (TVOCs) in waste gases
from non-combustion processes — Non-
dispersive infrared analyser equipped
with catalytic converter**

*Émissions de sources fixes — Détermination des composés organiques
volatils totaux (COV_Ts) dans les effluents gazeux des processus
sans combustion — Analyseur à infrarouge non dispersif équipé d'un
convertisseur catalytique*

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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 13199 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 1, *Stationary source emissions*.

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Introduction

Volatile organic compounds (VOCs) play significant roles in atmospheric chemistry, especially the formation of photochemical oxidants and/or ozone (O₃) and suspended particulate matter (SPM), which are known to have negative impacts on human health and biological systems. There are many areas of the world where their atmospheric concentrations are close to or above the level of the WHO guidelines for environmental standards in each nation. It is therefore strongly required in many nations to reduce the emission of VOC from various anthropogenic sources.

In order to manage VOC emission from stationary emission sources, it is essential for enterprises to evaluate the quantity of VOCs emitted from their facilities where organic solvents as well as other chemicals are used for industrial processes like painting, printing, cleaning, and degreasing.

A technique for continuously and precisely measuring the concentration of total VOCs (TVOCs) in waste gases emitted from ducts to atmosphere, which is easy to operate and to maintain, is very helpful for both governments and enterprises to control and reduce VOC emissions. This measurement method, based on the use of an NDIR analyser equipped with a catalytic converter for oxidation of TVOCs to CO₂, has some advantages compared to measurement methods using flame ionization detection (FID) and FID–GC (flame ionization detection–gas chromatography), namely:

- a) high-safety operation is possible, since no flame and no hydrogen are used;
- b) response factors of individual VOCs are not different from each other;
- c) no interference due to oxygen is observed.

Note, however, that this method is not applicable to waste gas from combustion processes.

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Stationary source emissions — Determination of total volatile organic compounds (TVOCs) in waste gases from non-combustion processes — Non-dispersive infrared analyser equipped with catalytic converter

1 Scope

This International Standard specifies the principle, the essential performance criteria and quality assurance/quality control (QA/QC) procedures of an automatic method for measuring total volatile organic compound (TVOC) content in waste gases of stationary sources, using a non-dispersive infrared absorption (NDIR) analyser equipped with a catalytic converter which oxidizes VOC to carbon dioxide.

This method is suitable for the measurement of TVOC emissions from non-combustion processes. This method allows continuous monitoring with permanently installed measuring systems, as well as intermittent measurements of TVOC emissions.

The method has been tested on field operation for painting and printing processes, where TVOC concentrations in the waste gases were from about 70 mg/m³ to 600 mg/m³.

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 for 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

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 TVOC mass concentrations passing through the duct.

3.2

analyser

analytical part in an extractive or *in situ* AMS

[ISO 12039:2001,^[3] 3.3]

3.3
calibration of an automatic measuring system
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

3.4
interference
negative or positive effect upon the response of the measuring system, due to a component of the sample that is not the measurand

3.5
interferent
interfering substance
substance present in the air mass under investigation, other than the measurand, that affects the response

[ISO 9169:2006, 2.1.12]

3.6
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]

3.7
mass concentration
concentration of a substance in a waste gas expressed as mass per volume

NOTE 1 Adapted from ISO 12039:2001,^[3] 3.10.

NOTE 2 Mass concentration is often expressed in milligrams per cubic metre (mg/m³).

3.8
measurand
particular quantity subject to measurement

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

EXAMPLE The TVOC mass concentration (mg/m³) in waste gas.

3.9
performance characteristic
one of the quantities assigned to equipment in order to define its performance

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

3.10
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.

3.11
residence time
time period for the sampled gas to be transported from the inlet of the probe to the inlet of the measurement cell

3.12**response time**

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]

3.13**span gas**

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

NOTE Adapted from ISO 12039:2001,^[3] 3.4.1.

EXAMPLE Normally a mixture of propane and air is used.

3.14**span point**

value of the output quantity (measured signal) of the automatic measuring system for the purpose of calibration, adjustment, etc. that represents a correct measured value generated by reference material

3.15**standard uncertainty**

uncertainty of the result of measurement expressed as a standard deviation

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

NOTE The standard uncertainty of a result of measurement is an estimate of the standard deviation of the population of all possible results of measurement which can be obtained by means of the same method of measurement for the measurand exhibiting a unique value.

3.16**total volatile organic compounds****TVOCs**

by convention, total organic compounds present with a partial pressure below their saturated vapour pressure at ambient air pressure and temperature

NOTE Measured TVOC values (mass concentration or volume concentration) are usually referred to carbon.

3.17**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]

3.18**zero gas**

gas or gas mixture used to establish the zero point on a calibration curve within a given concentration range

[ISO 12039:2001,^[3] 3.4.2]

3.19**zero point**

specified value of the output quantity (measured signal) of the AMS and which, in the absence of the measured component, represents the zero crossing of the calibration line

4 Symbols and abbreviated terms

γ TVOC mass concentration

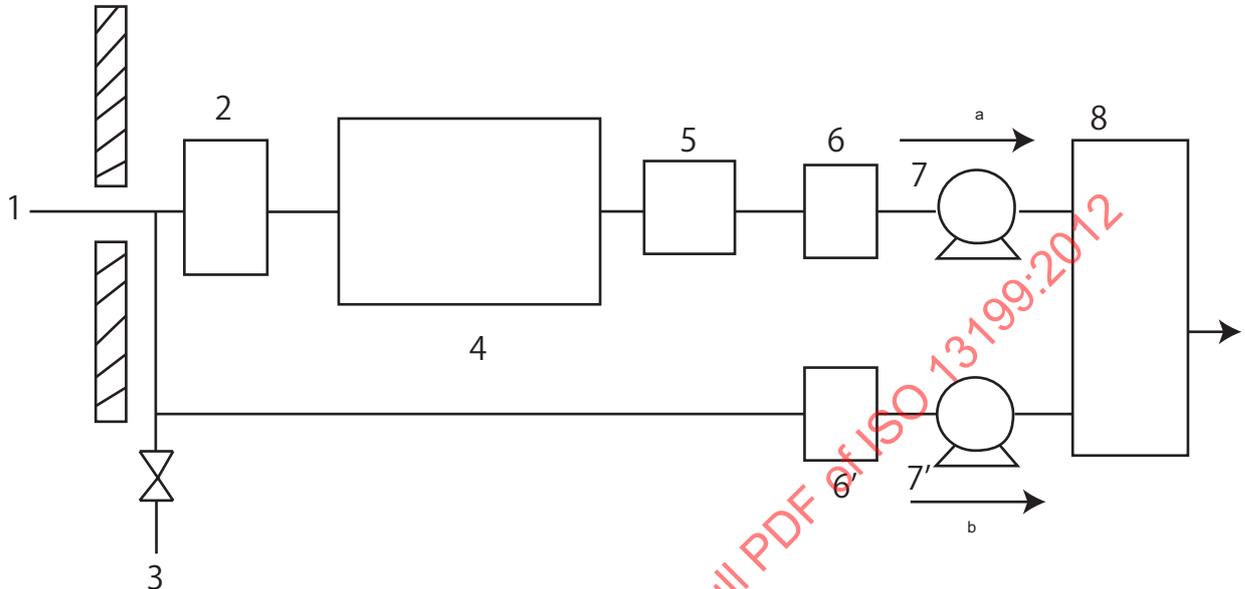
$\bar{\gamma}$	grand mean of measured TVOC mass concentration
φ	TVOC volume fraction (= 10^{-6})
e_i	residual (lack of fit) at level i
k	coverage factor
M_C	molar mass of carbon (= 12 g/mol)
n	number of measurements
s_j	standard deviation of level j
$s_{r,j}$	standard deviation of repeatability
$s_{R,j}$	standard deviation of reproducibility
u	standard uncertainty of TVOC mass concentration
$u(\gamma_{\text{TVOC}})$	combined uncertainty of TVOC mass concentration
$U(\gamma_{\text{TVOC}})$	expanded uncertainty of mass concentration
V_m	molar volume (22,4 l/mol)
$C_{V,r}$	coefficient of variation of repeatability
$C_{V,R}$	coefficient of variation of reproducibility
$C_{V,u}$	coefficient of variation of the standard uncertainty
\bar{x}	average of the measured values x_i
x_i	i th measured value
\bar{x}_i	average of the measured value at level i
\hat{x}_i	value estimated by the regression line at level i
AMS	automatic measuring system
NDIR	non-dispersive infrared absorption
QA	quality assurance
QC	quality control

5 Principle

5.1 Method of measurement

The measuring system consists of a sample conditioning system and the NDIR analyser for measuring CO₂ equipped with the converter for oxidation of TVOCs to CO₂ as shown in Figure 1. A portion of sample gas (gas A) passes through the converter (and the moisture removal system), and goes into the NDIR analyser, while another portion of sample gas (gas B) passes through (the moisture removal system), and goes into the NDIR analyser. The difference in the CO₂ concentration between gas A and gas B is equal to the concentration of CO₂ which comes from TVOCs.

The converter consists of oxidation catalyst such as platinum metal which is heated to around 450 °C for complete oxidation of TVOCs to CO₂. To avoid possible damage to the NDIR analyser due to halogens such as chlorine and/or chloride produced when halogenated organic compounds are oxidized, a halogen scrubber containing adsorbent is placed after the converter. Figure 1 shows an example of the measuring system including an NDIR analyser plus converter.



Key

- | | | | |
|---|--|-------|-------------------------|
| 1 | sampling probe, heated (if necessary) | 5 | halogen scrubber |
| 2 | particle filter (heated, if necessary) | 6, 6' | moisture removal system |
| 3 | zero and span gas inlet | 7, 7' | pump |
| 4 | converter | 8 | NDIR analyser |
| a | Gas A. | b | Gas B. |

Figure 1 — Diagram of the measuring system (example)

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 NDIR analyser containing the catalytic converter via the sampling probe, the particle filter and the sampling line. The sampling device, including the filter to remove fine particles that could affect the NDIR analyser, is heated to avoid sample condensation, if necessary.

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, polytetrafluoroethylene or polypropylene fluoride 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) have a filtering device upstream of the sampling line to trap all particles liable to impair the operation of the apparatus;
- d) have an inlet for applying zero and span gases at close to the entry nozzle of the sampling probe, upstream of the filter.

5.2 Analyser equipment

The gas analysers use, as the measurement principle, the absorption of infrared radiation (IR) by the component measured in characteristic wavelength ranges. The analysers operate according to the non-dispersive IR (NDIR) method, while the selectivity of measurement is achieved by the radiation detector which is filled with the component to be measured. Schematic diagrams of a typical NDIR analyser for measuring TVOC mass concentration are given in Figures A.1, A.2, and A.3.

5.3 Performance criteria fulfilment

5.3.1 General. The automatic measuring system (AMS) based on the NDIR method shall comply with the performance criteria specified in Table 1. The associated performance characteristics are determined as specified in 5.3.2 to 5.3.4.

5.3.2 General performance test. The manufacturer of the measuring system shall demonstrate in a general performance test that the relevant performance criteria listed in Table 1 are fulfilled by the instrument type. The procedure of this general performance test shall comply with the relevant standards.

5.3.3 Ongoing quality assurance (QA) and quality control (QC) in the laboratory. The user of 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.

5.3.4 Quality assurance during operation in the field. The user of AMS shall 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 gives an overview of the relevant performance characteristics and performance criteria of the analyser and measurement system to be evaluated at three levels, during a general performance test, by means of ongoing QA/QC in the laboratory and during field operation. In the rightmost column, values included in the calculation of the expanded uncertainty are indicated.

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. The procedures for the determination of these performance characteristics are described in Annex C.

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

The expanded 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 measurement uncertainty during field application shall be determined by the user of the measuring system in accordance with applicable international or national standards. It can be determined by a direct or an indirect

approach for uncertainty estimation as specified in ISO 20988. 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.

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 (laboratory) and field operation

Performance characteristic	Performance criterion	General performance test	QA/QC (lab)	Field operation	Term for evaluating uncertainty
Response time	≤120 s	✓	✓	✓	—
Standard deviation of repeatability in laboratory at zero point	≤1 % of the upper limit of the lowest measuring range used	✓	✓ ^a	—	✓
Standard deviation of repeatability in laboratory at span point	≤2 % of the upper limit of the lowest measuring range used	✓	✓ ^a	—	✓
Lack of fit	≤2 % of the upper limit of the lowest measuring range used	✓	✓	—	✓
Zero drift within 24 h	≤2 % of the upper limit of the lowest measuring range used	✓	—	✓	✓
Span drift within 24 h	≤2 % of the upper limit of the lowest measuring range used	✓	—	✓	✓
Influence of atmospheric pressure, for a pressure change of 2 kPa ^b	≤2 % of the upper limit of the lowest measuring range used	✓	—	—	✓
Influence of ambient temperature, for a change of 10 K	≤2 % of the upper limit of the lowest measuring range used	✓	—	—	✓
Influence of electric voltage for the variation per 10 V	≤2 % of the upper limit of the range per 10 V	✓	—	—	✓
Influence of CO ₂ and other interfering components ^c	≤4 % of the upper limit of the range used	✓	✓	—	✓
Converter efficiency, tested with CH ₄	≥95 %	✓	✓	—	✓
Losses and leakage in the sampling line and conditioning system	≤2 % of the measured value	—	—	✓	—
The upper limit of the lowest measuring range used should be set suitable to the application so that the measurement values lie within 20 %–80 % of the analyser range.					
^a Each zero gas and span gas containing 1 000 mg/m ³ of CO ₂ shall be used for ongoing QA/QC test in the laboratory.					
^b The tested pressure is defined in the manufacturer's recommendations.					
^c See C.5.					

6.2.3 Establishment of the uncertainty budget

An uncertainty budget shall be established to determine whether the analyser and its associated sampling system fulfil the requirements for a maximum allowable expanded uncertainty. This uncertainty budget shall be drawn up according to the procedures specified in ISO 14956 or ISO 20988, taking into account all the relevant characteristics included in calculation of expanded uncertainty given in Table 1. An example of the evaluation of an uncertainty budget is given in Annex D.

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 applied in ranges during the general performance test.

7.2 Choice of the measuring system

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

- a) temperature of the waste gas;
- b) water vapour content of the waste gas;
- c) dust load of the waste gas;
- d) expected concentration range of TVOCs;
- e) expected concentration of potentially interfering substances.

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. If there is a high dust loading in the sample gas, 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

7.3.1 Sampling location

The sampling location chosen for the measurement devices and sampling shall be of sufficient size and construction in order to obtain a representative emission measurement suitable for the measurement task. In addition, the sampling location shall be chosen with regard to safety of the personnel, accessibility and availability of electrical power.

7.3.2 Sampling point(s)

Ensure that the gas concentrations measured are representative of the average conditions inside the waste gas duct. Therefore, the sampling points shall be selected to allow for a representative sampling.

NOTE The selection of sampling points for representative sampling is described e.g. in ISO 9096^[2] and EN 15259.^[6]

7.4 Data collection

The values measured with the calibrated NDIR analyser under 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.

7.5 Calculation

The TVOC mass concentration at standard conditions is the quotient of the mass of TVOCs to the volume of the dry gas under specified reference conditions of temperature and pressure (273 K, 1 013 hPa), normally expressed in milligrams per cubic metre (mg/m³) which is calculated as carbon. Results of the measurement shall be expressed as mass concentrations at reference conditions of water vapour (dry gas).

If the TVOC concentration is provided as a volume concentration, Equation (1) shall be used to calculate the mass concentration at standard conditions of temperature and pressure (273 K, 1 013 hPa):

$$\gamma = \varphi \frac{M_C}{V_m} \quad (1)$$

where

φ is the TVOC volume fraction (= 10⁻⁶);

M_C is the molar mass of carbon (= 12 g/mol);

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

8 Quality assurance and quality control procedures

8.1 General

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

Two different applications of the automatic measuring system require distinction:

- AMS for intermittent measurements;
- permanently installed AMS for continuous monitoring.

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 C.

The user shall implement a procedure to guarantee that the zero gases and span gases used meet the uncertainty requirement specified in Annex B, 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 the 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. Appropriate safety procedures 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 NDIR analyser and set the zero;
- b) feed span gas and adjust the instrument accordingly;
- c) feed zero gas into the NDIR analyser once more and check the reading returns to zero.

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

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
Standard deviation of repeatability at zero point	once a year	once a year
Standard deviation of repeatability 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 e.g. in legislation or applicable standards by comparison with an independent method of measurement
Check of CO ₂ influence	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
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.

8.3.2.2 Response time

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

8.3.2.3 Standard deviation of repeatability at zero point

The standard deviation of repeatability at zero point shall be checked in accordance with C.3.2 at least once a year.

8.3.2.4 Standard deviation of repeatability at span point

The standard deviation of repeatability at span point shall be checked in accordance with C.3.3 at least once a year.

8.3.2.5 Check of lack of fit (linearity check)

The linearity of the AMS response shall be checked in accordance with C.4 at least once a year.

8.3.2.6 Check of CO₂ influence

The CO₂ influence shall be checked in accordance with C.5 at least once a year.

8.3.2.7 Check of the converter efficiency

The converter efficiency shall be checked in accordance with C.6 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 C.7 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 C.8 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 the relevant standards shall be observed.

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 C.2 at least once a year.

8.4.2.3 Standard deviation of repeatability at zero point

The standard deviation of repeatability at zero point shall be checked in accordance with C.3.2 at least once a year.

8.4.2.4 Standard deviation of repeatability at span point

The standard deviation of repeatability at span point shall be checked in accordance with C.3.3 at least once a year.

8.4.2.5 Check of lack of fit (Linearity check)

The linearity of the AMS response shall be checked in accordance with C.4 at least once a year.

8.4.2.6 Check of CO₂ influence

The CO₂ influence shall be checked in accordance with C.5 at least once a year.

8.4.2.7 Check of the converter efficiency

The converter efficiency shall be checked in accordance with C.6 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 C.7 at least once a year.

8.4.2.9 Zero and span drift

The zero and span drift shall be checked in accordance with C.8 at least once in the period of unattended operation. This manual check is also needed for AMS with internal automatic zero and span checks.

8.4.2.10 Regular maintenance of the analyser

The regular maintenance of the analyser shall be performed once in the period of unattended operation according to the manufacturer's instructions and documentation.

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 The continuous flame ionization detector method for the determination of TVOC mass concentration in waste gases specified in EN 13526^[5] may 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 the relevant 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 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.

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 13199:2012);
- b) description of the measurement objective;
- c) principle of gas sampling;
- d) information about the analyser and description of the sampling and conditioning line;
- e) identification of the analyser used, and the performance characteristics of the analyser 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 this International Standard.

Annex A (informative)

Schematic diagrams of NDIR analysers

A.1 General

Schematic diagrams of NDIR analysers for measuring TVOCs are shown in Figures A.1, A.2, and A.3, respectively. Type 1 has a flowing reference cell through which the TVOC sample gas (no converter, gas B) passes. Type 2 has a reference cell which is filled with a non-IR absorbent gas and has a switch valve. Type 3 has a modulation valve with a single cell.

A.2 Schematic diagram for NDIR analyser — Type 1

A schematic diagram of a flowing reference cell type NDIR analyser (dual beam) is shown in Figure A.1. This analyser consists of the reference cell and sample cell. A modulating unit (label 2) between IR source (label 1) and cells (labels 3 and 4) guides the light path through either the sample cell or the reference cell resulting in an alternating signal characteristic (at least for different CO₂ concentrations). In order to identify the TVOC concentration in the sample gas, a part of the sample gas stream is guided through a converter (TVOCs → CO₂) and continuously fed into as gas A. The reference cell is continuously purged with sample gas containing TVOCs (no converter, gas B). The difference in CO₂ concentration between both cells correlates with the TVOC concentration in the sample.

A.3 Schematic diagram for NDIR analyser — Type 2

A schematic diagram of a switch valve type NDIR analyser (dual beam) is shown in Figure A.2. This analyser consists of the reference cell and sample cell. The reference cell (label 3) is filled with the gas which does not absorb the IR radiation. The IR radiation passes through the reference cell and the sample cell (label 4) simultaneously to obtain the alternation current of IR intensities. The difference in the alternating current for IR intensities between the sample cell and the reference cell is the output signal. In order to identify the TVOC concentration in the sample gas, gas A and gas B feed into the sample cell alternately by using the switch valve (label 9) at a specific period such as 5 s to determine both CO₂ signals of gas A and gas B. The difference between the signal of gas A and the signal of gas B correlates to the TVOC concentration present in the sample. A single beam-type NDIR analyser of type 2 is also manufactured.

A.4 Schematic diagram for NDIR analyser — Type 3

A schematic diagram of a modulation valve-type NDIR analyser (single beam) is shown in Figure A.3. There is no optical modulation unit (chopper). Gas A and gas B feed into the sample cell (label 2) alternately by using the modulation valve (label 7) at a specific very short period such as 1 Hz to determine a modulation signal. This modulation signal, influenced by both signals of gas A and gas B, is rectified to obtain the difference in the signal between gas A and gas B directly. There are also dual beam-type NDIR analysers of type 3.

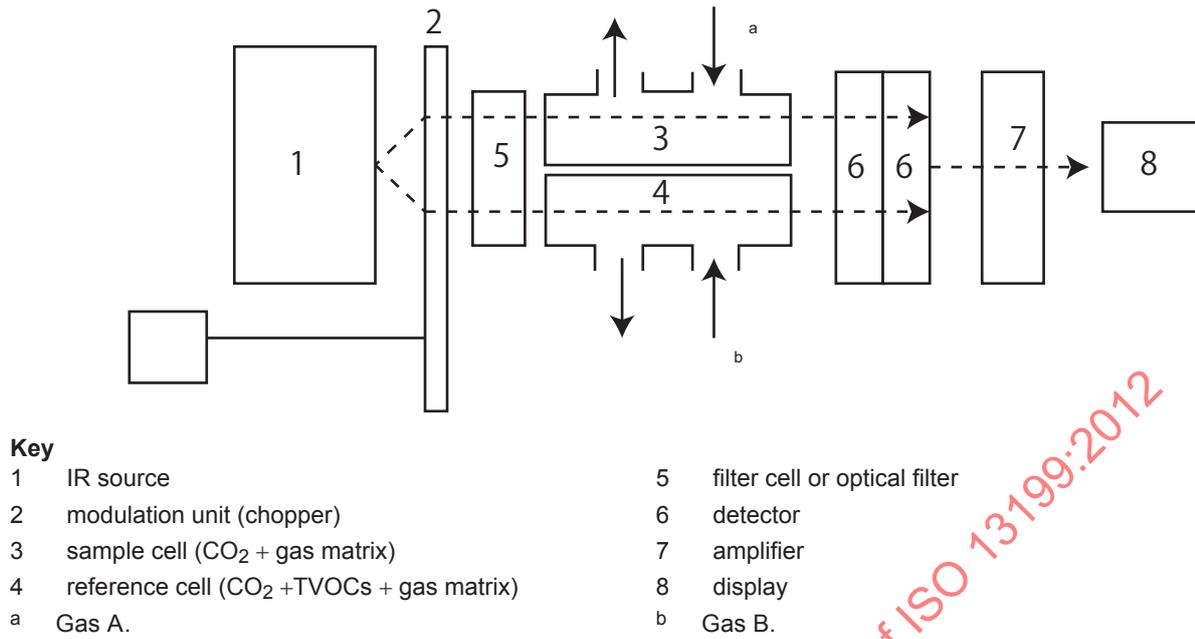


Figure A.1 — Diagram of a flowing reference cell type NDIR analyser (dual beam)

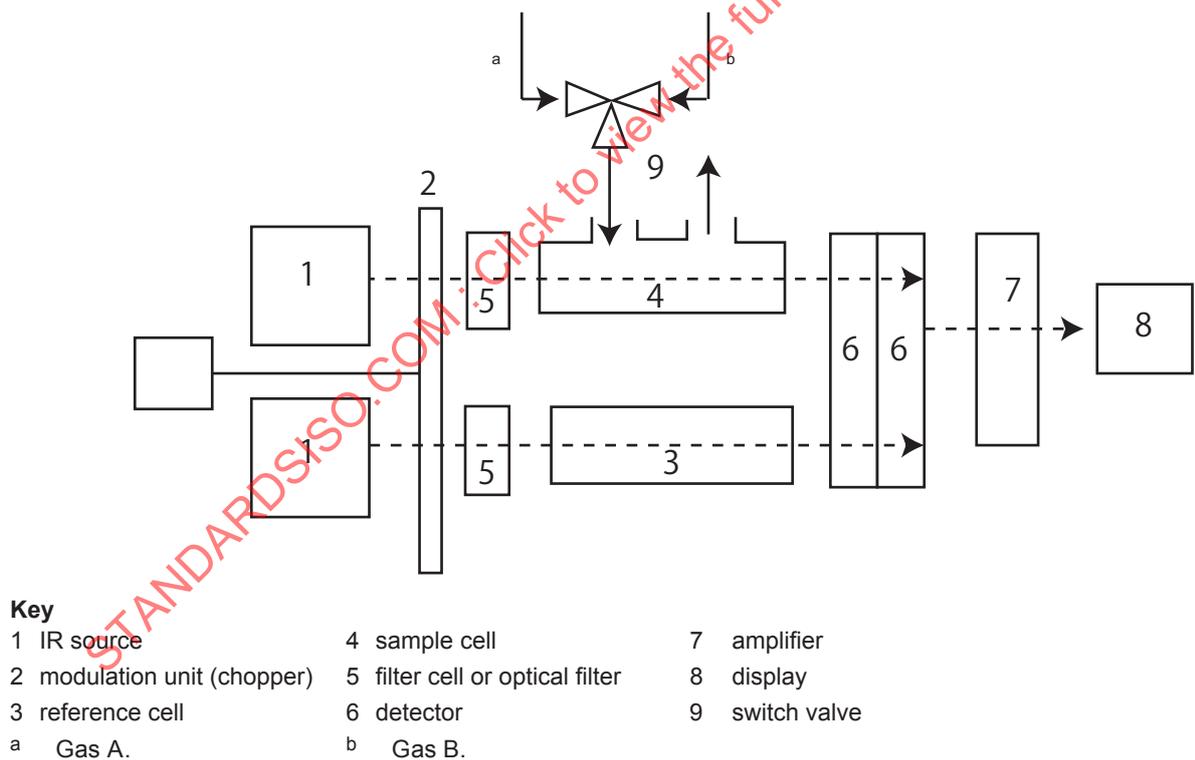
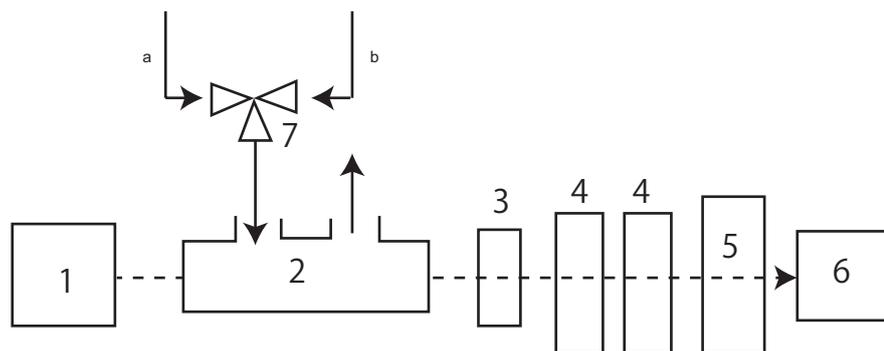


Figure A.2 — Diagram of a switch valve type NDIR analyser (dual beam)



Key

- | | | | |
|---|-------------------------------|---|------------------|
| 1 | IR source | 5 | amplifier |
| 2 | sample cell | 6 | display |
| 3 | filter cell or optical filter | 7 | modulation valve |
| 4 | detector | | |
| a | Gas A. | b | Gas B. |

Figure A.3 — Diagram of a modulation valve type NDIR analyser (single beam)

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Annex B (normative)

Operational gases

B.1 General

Several operational gases are required when using this International Standard. See Tables B.1 and B.2.

B.2 Zero gas

B.2.1 The zero gas shall consist of synthetic air. The carbon content should not exceed 1,0 % of the upper limit of the measuring range used.

B.2.2 The zero gas used for the ongoing QA/QC test in the laboratory shall contain 1 000 mg/m³ of CO₂.

B.3 Span gas

B.3.1 Span gas shall consist of propane in synthetic air. It shall have a known concentration with a maximum permissible expanded uncertainty of 2,0 % of its nominal value traceable to national standards.

B.3.2 The span gas concentration should be about 70 % of the selected measuring range.

B.3.3 The span gas used for the ongoing QA/QC test the laboratory shall contain 1 000 mg/m³ of CO₂.

B.4 Reference gas

B.4.1 Reference gas shall consist of propane in synthetic air. It shall have a known concentration with a maximum permissible expanded uncertainty of 1,0 % of its nominal value traceable to national standards.

B.4.2 The reference gas concentration should be about 70 % of the selected measuring range.

B.5 Test gas for checking converter efficiency

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

B.6 Test gas for checking the influence of carbon dioxide

Test gas for checking the effect of carbon dioxide shall consist of carbon dioxide and propane in synthetic air. The concentration of carbon dioxide shall be 2 000 mg/m³ and that of propane shall be around 450 mg/m³.

Table B.1 — List of gases for the general performance test

Zero gas	Synthetic air Carbon content <1,0 % of the upper limit of the measuring range used
Span gas	Propane in synthetic air Concentration about 70 % of the selected measuring range
Reference gas	Ppropane in synthetic air (expanded uncertainty of 1,0 %)

Table B.2 — List of gases for the ongoing QA/QC test in the laboratory

Zero gas	Synthetic air containing 1 000 mg/m ³ of CO ₂
Span gas	To consist of propane in synthetic air concentration (about 70 % of the selected measuring range) containing 1 000 mg/m ³ of CO ₂

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Annex C (normative)

Procedures for determination of the performance characteristics during the general performance test

C.1 General

Before any tests are performed, the warm-up time specified by the manufacturer shall be taken into account. If the warm-up time is not specified, a minimum of 2 h should be taken.

Before determining the performance characteristics of an NDIR analyser, the instrument shall be set up according to the procedure specified in 8.3.2.

Under test conditions for each individual performance characteristic, the values of the following parameters shall be constant within the specified range stated below:

- surrounding temperature: ± 2 °C;
- sampling pressure: $\pm 0,2$ kPa;
- supply voltage: ± 1 % of the nominal line voltage (except for the voltage dependence test).

For the determination of the various performance characteristics, reference gases with a known uncertainty of concentration shall be used.

C.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 used measuring range. The zero and test gas shall be applied to the NDIR analyser 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 by summing the lag time and the rise time in the rising mode, and by summing 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, take the longer of the two for computation of the response time.

For instruments where transient oscillations occur in approach to the final output signal, the final output signal is considered to be 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 used measuring range to the NDIR analyser at the sample gas inlet.

C.3 Repeatability at zero and at span level

C.3.1 General

To determine repeatability at zero and at span level, several measurements are repeated at zero and at a span concentration. Standard deviation and repeatability are calculated for both series of measurement (zero and span value) according to ISO 9169.

C.3.2 Standard deviation of repeatability at zero point

The standard deviation of repeatability at zero point shall be determined by application of a reference material at the zero point (zero gas). First adjust the zero point of the NDIR analyser. Then zero gas has to be applied at the zero and span gas inlet (see Figure 1). For the ongoing QA/QC test in the laboratory, the zero gas containing 1000 mg/m³ of CO₂ shall be used.

If the standard deviation of repeatability 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 standard deviation of repeatability at zero point using Equation (C.1):

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

where

s_r is the standard deviation of repeatability;

x_i is the i th measured value;

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

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

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

C.3.3 Standard deviation of repeatability at span point

The standard deviation of repeatability at span point shall be determined by application of a reference material at the span point (span gas). For the ongoing QA/QC test in the laboratory, the span gas containing 1000 mg/m³ of CO₂ shall be used.

If the standard deviation of repeatability 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 a time equivalent to one independent reading and then recording 20 consecutive individual readings. The measured signals obtained shall be used to determine the standard deviation of repeatability at span using Equation (C.1).

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

C.4 Check of lack of fit (linearity check)

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

Perform for each test gas with the accepted value 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 AMS (x values) and the test gas values (γ values). In the next step, the

average \bar{x}_i of AMS 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 (C.2):

$$e_i = |\hat{x}_i - \bar{x}_i| \quad (\text{C.2})$$

where

e_i is the residual (lack of fit) at level i ;

\bar{x}_i is the average of the measured value at level i ;

\hat{x}_i is the value estimated by the regression line at level i .

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 shall be corrected until the performance criterion is met.

C.5 Check of CO₂ influence

Since this International Standard uses the NDIR method for measurement of CO₂ which derives from TVOCs, compounds that have infrared absorption can interfere with the measurement. However, this method is applied to the measurement of TVOCs in waste gases from non-combustion processes, and thus most of typical interferences such as SO₂, NO_x, and CO are not likely to be present. Since the waste gas without combustion is usually at a little higher than ambient temperature and does not contain much water, the influence of water is considered negligible. The influence of TVOCs which are present in the reference cell (Figure A.1) is considered negligibly small, since most VOCs do not have any absorption around the wavelength of 4,2 μm (which is used for measurement of CO₂ concentration).

Only relatively high concentrations of CO₂ (up to 2 000 mg/m³) affect the measurement.

To test the influence of any CO₂ present, a gas mixture of known concentrations of propane, γ_{std} , and CO₂ (around 2 000 mg/m³) in air is used. The test gas is analysed with the AMS and then the concentration of propane, γ_{obs} , is determined. The influence coefficient, c_{int} , is calculated according to Equation (C.3):

$$c_{\text{int}} = \frac{\gamma_{\text{obs}} - \gamma_{\text{std}}}{\gamma_r} \times 100 \% \quad (\text{C.3})$$

where

γ_{obs} is the concentration of propane measured with analyser;

γ_{std} is the known propane concentration in the propane and CO₂ gas mixture;

γ_r is the measurement range.

The influence of the CO₂ shall meet the appropriate performance criterion specified in Table 1.

C.6 Check of converter efficiency

The converter efficiency shall be checked with a test gas containing methane at a concentration of about 70 % of the upper limit of the range, which is fed into the analyser, and shall comply with Table 1.

After the zero and span check of the analyser, a test gas containing methane at a concentration of $\gamma_{\text{CH}_4, \text{test}}$ is introduced to the analyser and the measured concentration value, $\gamma_{\text{CH}_4, \text{meas}}$, is recorded.

The converter efficiency, η_{conv} , is calculated according to Equation (C.4):

$$\eta_{\text{conv}} = \frac{\gamma_{\text{CH}_4, \text{meas}}}{\gamma_{\text{CH}_4, \text{test}}} \times 100 \% \quad (\text{C.4})$$

The value of the efficiency shall meet the appropriate performance criterion specified in Table 1.

C.7 Sampling system and leakage check

A check of the sampling system shall be carried out before each measurement series.

The sampling system shall be checked for leaks.

The entire measuring system shall be checked by supplying zero gas and test gas directly at the sampling probe by repeating steps a) to c) of 8.3.2.1. The test gas should have a propane concentration of about 70 % of the measuring range. Small deviations shall be corrected. Large deviations indicate malfunctions. The causes shall be identified and eliminated. Then the measuring system shall be checked again.

Loss and leakage shall meet the appropriate performance criterion specified in Table 1.

C.8 Zero drift and span drift

Zero and span drifts are estimated by applying at least 10 sequences of zero and span level, evenly distributed over a period of 24 h, and calculating the slope of a linear regression for each concentration, according to ISO 9169.

The position of the zero point and of the span point shall be determined manually by feeding zero gas and span gas. The deviations between the measured values at the zero point and at the span point and the nominal values shall meet the performance criterion specified in Table 1.

Annex D (informative)

Example of assessment of compliance of the NDIR method

D.1 Specific conditions in the site

This annex gives an example of assessment of compliance of the NDIR method for TVOCs with requirements on emission measurements. Specific on-site conditions are given in Table D.1.

Table D.1 — Site-specific conditions

Specific conditions	Value/range
Range of analyser (TVOCs)	0 mg/m ³ to 600 mg/m ³
Studied concentration of TVOCs	up to around 600 mg/m ³
Conditions in the field	Value/range
Sample volume flow	(60 ± 6) l/h
Temperature during adjustment	300 K
Fluctuations in ambient temperature during measurement	283 K to 308 K
Voltage range	100 V to 110 V
Atmospheric pressure during adjustment	100 kPa
Atmospheric pressure variation	<1 kPa
CO ₂ concentration range in the field	1 000 mg/m ³ to 2 000 mg/m ³
Reference gas	~450 mg/m ³ ± 1 %

D.2 Performance characteristics of the method — Results of validation of the tests

The results of validation of the tests with regard to performance characteristics of the method are given in Table D.2.

D.3 Calculation of standard uncertainty of measurement values given by the analyser

D.3.1 General

Model equations in this clause, as well as calculations of partial uncertainties are related to the values measured by the analyser and expressed in mg/m³. Explanation and calculation procedures for the standard uncertainty associated with measurement are given in ISO 20988.

D.3.2 Model equation and application of rule of uncertainty propagation

The mass concentration of TVOCs, γ_{TVOCs} , e.g. in milligrams per cubic metre, is equal to the concentration given by the analyser plus corrections due to deviations associated with influence quantities and the performance characteristics of the analyser. See Equation (D.1):

$$\gamma_{\text{TVOCs}} = \gamma_{\text{read}} + \delta c_{\text{lof}} + \delta c_{\text{d},0} + \delta c_{\text{d},s} + \delta c_r + \delta c_{\text{adj}} + \delta c_i + \sum_{j=1}^p \delta c_{\text{inf},j} \quad (\text{D.1})$$

where

γ_{read} is the mass concentration of TVOCs given by the analyser;

- δc_{lof} is the correction for lack of fit;
- $\delta c_{d,0}$ is the correction for zero drift ;
- $\delta c_{d,s}$ is the correction for span drift;
- δc_r is the correction for repeatability of the measurement;
- δc_{adj} is the correction for adjustment;
- δc_i is the correction for influence (CO₂);
- $\delta c_{inf,j}$ is the correction for influence quantities (e.g. ambient temperature, atmospheric pressure, sample volume flow, voltage).

D.3.3 Results of uncertainty calculation

Quantification of the impact of selected performance characteristics as partial standard uncertainty is calculated in accordance with ISO 14956. See Table D.3.

Table D.2 — Performance characteristics

Performance characteristic	Performance criterion	Results of laboratory test
Response time	≤120 s	60 s (20 s to 90 s)
Standard deviation of repeatability in laboratory at zero point	≤1 % of the upper limit of the lowest measuring range used	0,2 % (0,1 % to 0,2 %)
Standard deviation of repeatability in laboratory at span point	≤2 % of the upper limit of the lowest measuring range used	0,4 % (0,2 % to 0,5 %)
Lack of fit	≤2 % of upper limit of the lowest measuring range used	0,5 % (−0,3 % to −0,6 %)
Zero drift in 24 h	≤2 % of upper limit of the lowest measuring range used	0,6 % (0,1 % to 1,0 %)
Span drift in 24 h	≤2 % of upper limit of the lowest measuring range used	0,7 % (0,3 % to 1,0 %)
Influence of atmospheric pressure for a pressure change of 2 kPa ^a	≤2 % of upper limit of the lowest measuring range used	— ^b
Influence of ambient temperature, for a change of 10 K	≤2 % of upper limit of the lowest measuring range used	— ^b
Influence of electric voltage	≤2 % of the range per 10V	— ^b
Influence of CO ₂ and other interfering components ^c CO ₂ (2 000 mg/m ³)	within ±4 % of the range	−1,4 % (−2 % to −0,8 %)
Converter efficiency, tested with CH ₄	≥95 %	about 100 %
Losses and leakage in the sampling line and conditioning system	≤2 % of upper limit of the lowest measuring range used	≤2 %

^a The tested pressure is defined in the manufacturer's recommendations.

^b Use the values empirically estimated and/or specified by the manufacturer. See Table D.3.

^c Influences (carbon dioxide) that shall be tested are at least those given in Table 2.