
**Stationary source emissions —
Determination of the mass
concentration of carbon monoxide,
carbon dioxide and oxygen in flue
gas — Performance characteristics of
automated measuring systems**

*Émissions de sources fixes — Détermination de la concentration
de monoxyde de carbone, de dioxyde de carbone et d'oxygène —
Caractéristiques de fonctionnement et étalonnage de systèmes
automatiques de mesure*

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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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

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

This second edition cancels and replaces the first edition (ISO 12039:2001), which has been technically revised. The main changes compared to the previous edition are as follows:

- The structure and the components are changed to be similar to the latest ISO standards; ISO 17179 (measurement of NH₃), ISO 13199 (measurement of total VOC), ISO 25140 (measurement of CH₄), ISO 21258 (measurement of N₂O) and others.
- Addition or deletion and change in terms and definitions.
- Addition of a new analytical technique (tunable laser spectroscopy) for in-situ measurement of CO, CO₂ and O₂
- The performance characteristics and criteria as well as QA/QC procedures are changed to harmonize with latest ISO standards.
- Examples of performance test results and the results of uncertainty calculation are shown for CO, CO₂ and O₂ measurement.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Carbon monoxide, carbon dioxide, and oxygen are gases found in the exhaust gases of combustion processes. Determination of the concentration of these gases is necessary to demonstrate compliance with local regulations and can assist the operator in the optimization of the combustion process. The determination of O₂ and/or CO₂ is also necessary to normalize the measured concentration of other gases and dusts to defined conditions. There are a number of ways to measure concentrations of CO, CO₂ and O₂ in stacks/ducts.

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Stationary source emissions — Determination of the mass concentration of carbon monoxide, carbon dioxide and oxygen in flue gas — Performance characteristics of automated measuring systems

1 Scope

This document specifies the fundamental structure and the most important performance characteristics of automated measuring systems for carbon monoxide (CO), carbon dioxide (CO₂) and oxygen (O₂) to be used on stationary source emissions. This document describes methods and equipment for the measurement of concentrations of these gases.

The method allows continuous monitoring with permanently installed measuring systems of CO, CO₂ and O₂ emissions. This international standard describes extractive systems and in situ (non-extractive) systems in connection with analysers that operate using, for example, the following principles:

- infrared absorption (CO and CO₂);
- paramagnetism (O₂);
- zirconium oxide (O₂);
- electrochemical cell (O₂);
- tuneable laser spectroscopy (TLS) (CO, CO₂ and O₂).

Other instrumental methods can be used provided they meet the minimum requirements proposed in this document.

Automated measuring systems (AMS) based on the principles above have been used successfully in this application for measuring ranges which are described in [Annex G](#).

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 14956, *Air quality — Evaluation of the suitability of a measurement procedure by comparison with a required measurement uncertainty*

3 Terms and definitions

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

3.1

analyser

analytical part in an extractive or *in situ* AMS ([3.3](#))

3.2
automated measuring system
AMS

measuring system interacting with the flue gas under investigation, returning an output signal proportional to the physical unit of the *measurand* (3.8) in unattended operation

[SOURCE: ISO 9169:2006, 2.1.2 modified]

Note 1 to entry: In the sense of this document, an AMS is a system that can be attached to a duct or stack to continuously or intermittently measure the mass concentration of CO, CO₂ and O₂ passing through the duct.

3.3
in situ AMS

non-extractive systems that measure the concentration directly in the duct or stack

Note 1 to entry: In situ systems measure either across the stack or duct or at a point within the duct or stack.

3.4
parallel measurements

measurements taken on the same duct in the same sampling plane for the same period of time with the *AMS* (3.2) under test and with the *reference method* (3.12) at points a short distance from each other, providing pairs of measured values

3.5
interference
cross-sensitivity

negative or positive effect upon the response of the measuring system, due to a component of the sample that is not the *measurand* (3.8)

3.6
interferent
interfering substance

substance present in the air mass under investigation, other than the *measurand* (3.8), that affects the response of *AMS* (3.2)

3.7
lack-of-fit

systematic deviation within the range of application between the measurement results obtained by applying the calibration function to the observed response of the measuring system, measuring *reference materials* (3.11) and the corresponding accepted value of such *reference materials* (3.11)

Note 1 to entry: Lack-of-fit may be a function of the measurement result.

Note 2 to entry: The expression “lack-of-fit” is often replaced in everyday language for linear relations by “linearity” or “deviation from linearity”.

[SOURCE: ISO 9169:2006, 2.2.9]

3.8
measurand

particular quantity subject to measurement

[SOURCE: ISO/IEC Guide 98 3:2008, B.2.9, modified — Example and Note removed.]

3.9
performance characteristic

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

Note 1 to entry: 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* (3.9) remain within a predefined range without external servicing, e.g. refill, adjustment

[SOURCE: ISO 9169:2006, 2.2.11]

Note 1 to entry: The period of unattended operation is often called maintenance interval.

3.11**reference material**

substance or mixture of substances with a known concentration within specified limits, or a device of known characteristics

Note 1 to entry: Normally calibration gases, gas cells, gratings or filters are used.

[SOURCE: ISO 14385-1:2014]

3.12**reference method**

measurement method taken as a reference by convention, which gives the accepted reference value of the *measurand* (3.8)

3.13**transport time**

<measuring system> time period for transportation of the sampled gas from the inlet of the probe to the inlet of the measurement instrument

3.14**response time**

time interval between the instant when a stimulus is subjected to bring about 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

[SOURCE: ISO 9169:2006, 2.2.4]

Note 1 to entry: Lag time, rise time and fall time are defined in ISO 9169:2006.

3.15**span gas**

gas or gas mixture used to adjust and check the span point on the response line of the measuring system

Note 1 to entry: This concentration is often chosen around 70 % to 90 % of full scale.

3.16**span point**

value of the output quantity (measured signal) of the *automated measuring system* (3.2) for the purpose of calibration, adjustment, etc. that represents a correct measured value generated by reference gas

3.17**standard uncertainty**

uncertainty (3.18) of the result of a measurement expressed as a standard deviation

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

3.18**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* (3.8)

[SOURCE: ISO/IEC Guide 98 3:2008, 2.2.3, modified — Note 1,2 and 3 removed.]

3.19

validation of automated measuring system

procedure to check the statistical relationship between values of the *measurand* (3.8) indicated by the *automated measuring system* (3.2) and the corresponding values given by *parallel measurements* (3.4) implemented simultaneously at the same measuring point

3.20

zero gas

gas or gas mixture used to establish the *zero point* (3.21) on a calibration curve within a given concentration range

3.21

zero point

specified value of the output quantity (measured signal) of the *AMS* (3.2) and which, in the absence of the measured component, represents the zero crossing of the calibration line. In case of O_2 monitoring *AMS* (3.2), the zero point is interpreted as the lowest measurable value.

4 Symbols and abbreviated terms

| | |
|---------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------|
| e_i | Residual (lack-of-fit) at level i |
| K | Coverage factor |
| N | Number of measurements |
| s_r | Standard deviation of repeatability |
| $u(\gamma_X)$ | Combined uncertainty of X (CO, CO ₂ or O ₂) mass concentration |
| $U(\gamma_X)$ | Expanded uncertainty of X (CO, CO ₂ or O ₂) mass concentration |
| M_x | Molar mass of X (CO, CO ₂ or O ₂ , g/mol) |
| V_M | Molar volume (22,4 l/mol at standard conditions) |
| φ_X | Volume fraction of X (CO, CO ₂ or O ₂) |
| γ_X | X (CO, CO ₂ or O ₂) mass concentration in mg/m ³ |
| γ_s | CO, CO ₂ or O ₂ mass concentration at standard conditions in mg/m ³ (273,15 K; 101,325 kPa) |
| γ_R | CO, CO ₂ or O ₂ mass concentration at reference conditions in mg/m ³ (273,15 K; 101,325 kPa; H ₂ O corrected) |
| \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 |
| \dot{x}_i | Value estimated by the regression line at level i |
| AMS | Automated measuring system |
| FTIR | Fourier transform infrared |
| GFC | Gas filter correlation |

| | |
|------|-----------------------------|
| NDIR | Non-dispersive infrared |
| QA | Quality assurance |
| QC | Quality control |
| TLS | Tuneable laser spectroscopy |

5 Principle

This document describes automated measurement systems for sampling, sample conditioning, and determining CO, CO₂ and O₂ content in flue gas using instrumental methods (analysers).

There are two types of automated measuring systems:

- extractive systems;
- in situ systems.

With extractive systems, the representative gas sample is taken from the stack with a sampling probe and conveyed to the analyser through the sampling line and sample gas conditioning system.

In situ systems do not require any sample processing. For the installation of these systems, a representative place in the stack is to be chosen.

The systems described in this document measure CO, CO₂ and O₂ concentrations using instrumental methods that shall meet the minimum performance specifications given.

This document specifies performance characteristics and criteria for AMS.

6 Description of the automated measuring systems

6.1 Sampling and sample gas conditioning systems

Sampling and sample gas conditioning systems for extractive and in situ methods shall conform to ISO 10396.

In extractive sampling, these gases are conditioned to remove aerosols, particulate matter and other interfering substances before being conveyed to the instruments. Three kinds of extractive systems:

- a) Cold-dry,
- b) Hot-wet, and
- c) Dilution,

as well as non-extractive systems, are described in ISO 10396. In non-extractive sampling, the measurements are made in situ; therefore, no sample conditioning other than filtering of filterable materials at the probe tip is required.

The details of the extractive sampling and sample gas conditioning systems as well as analyser equipment are described in [Annex A](#) and [Annex B](#). In [Annex C](#), two kinds of in situ systems are illustrated.

6.2 Analyser equipment

Examples of the typical analytical methods available are described in the [Annex A](#), [Annex B](#) and [Annex C](#).

AMS shall meet the performance characteristics described in [Clause 7](#).

7 Performance characteristics and criteria

7.1 Performance criteria

[Table 1](#) gives the performance characteristics and performance criteria of the analyser and measurement system to be evaluated during performance tests, by means of ongoing QA/QC in the laboratory and during field operation. Test procedures for the performance test are specified in [Annex E](#).

Table 1 — Performance characteristics and criteria of AMS for measurement of CO, CO₂ and O₂

| Performance characteristic | Performance criterion | | Test procedure |
|-----------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------|-------------------------------------------------------------|-----------------------|
| | CO and CO ₂ | O ₂ | |
| Response time | ≤200 s | ≤200 s | E.2 |
| Standard deviation of repeatability at zero point | ≤2,0 % of the upper limit of the lowest measuring range used ^a | ≤0,2 % for O ₂ volume concentration ^b | E.3.2 |
| Standard deviation of repeatability at span point | ≤2,0 % of the upper limit of the lowest measuring range used | ≤0,2 % for O ₂ volume concentration | E.3.3 |
| Lack-of-fit (linearity) | ≤2,0 % of the upper limit of the lowest measuring range used | ≤0,2 % for O ₂ volume concentration | E.4 |
| Zero drift within 24 h | ≤2,0 % of the upper limit of the lowest measuring range used | ≤0,2 % for O ₂ volume concentration | E.8 |
| Span drift within 24 h | ≤2,0 % of the upper limit of the lowest measuring range used | ≤0,2 % for O ₂ volume concentration | E.8 |
| Zero drift within the period of unattended operation | ≤3,0 % of the upper limit of the lowest measuring range used | ≤0,2 % for O ₂ volume concentration | E.9 |
| Span drift within the period of unattended operation | ≤3,0 % of the upper limit of the lowest measuring range used | ≤0,2 % for O ₂ volume concentration | E.9 |
| Sensitivity to sample gas pressure, for a pressure change of 2 kPa | ≤3,0 % of the upper limit of the lowest measuring range used | ≤0,2 % for O ₂ volume concentration | E.11 |
| Sensitivity to sample gas flow for extractive AMS | ≤2,0 % of the upper limit of the lowest measuring range used | ≤0,2 % for O ₂ volume concentration | E.12 |
| Sensitivity to ambient temperature, for a change of 10 K in the temperature range specified by the manufacturer | ≤3,0 % of the upper limit of the lowest measuring range used | ≤0,3 % for O ₂ volume concentration | E.13 |

^a Percentage value as percentage of the upper limit of the lowest measuring range used.

^b Percentage value as oxygen volume concentration (volume fraction).

Table 1 (continued)

| Performance characteristic | Performance criterion | | Test procedure |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------|------------------------------------------------|------------------------------------------------------------------|
| | CO and CO ₂ | O ₂ | |
| Sensitivity to electric voltage in the voltage range specified by the manufacturer | ≤2,0 % of the upper limit of the lowest measuring range used per 10V | ≤0,2% for O ₂ volume concentration | E.14 |
| Cross-sensitivity | ≤4,0 % of the upper limit of the lowest measuring range used | ≤0,4 % for O ₂ volume concentration | E.5 |
| Losses and leakage in the sampling line and conditioning system | ≤2,0 % of the measured value | | E.6 for loss and E.7 for leakage |
| Excursion of the measurement beam of cross-stack in situ AMS | ≤2,0 % of the measured value of the lowest measuring range used | | E.10 |
| ^a Percentage value as percentage of the upper limit of the lowest measuring range used. ^b Percentage value as oxygen volume concentration (volume fraction). | | | |

The measuring range is defined by two values of the measurand, or quantity to be supplied, within which the limits of uncertainty of the measuring instrument are specified. The upper limit of the lowest measuring range used should be set suitable to the application such that the measurement values lie within 20 % to 80 % of the measuring range.

7.2 Determination of the performance characteristics

7.2.1 Performance test

The performance characteristics of the AMS shall be determined during the performance tests described in [Annex E](#). The values of the performance characteristics determined shall meet the performance criteria specified in [Table 1](#).

The ambient conditions applied during the performance tests shall be documented.

The measurement uncertainty of the AMS measured values shall be calculated in accordance with ISO 14956 on the basis of the performance characteristics determined during the performance test and shall meet the level of uncertainty appropriate for the intended use. These characteristics may be determined either by the manufacturer or by the user.

7.2.2 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. For process monitoring (non-regulatory application), the level of uncertainty shall be appropriate for the intended use. It can be determined by a direct or an indirect approach for uncertainty estimation as described 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:

- the sampling line and conditioning system,
- the site-specific conditions, and
- the calibration gases used.

8 Selection and installation procedure

8.1 Choice of the measuring system

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

- ambient temperature range;
- temperature range of the flue gas;
- water vapour content of the flue gas;
- dust loading of the gases;
- expected concentration range of CO, CO₂ and O₂;
- expected concentration of potentially interfering substances;

To avoid long response time 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 monitoring emissions, the user shall verify that the necessary QA/QC procedures have been performed.

NOTE Information on QA/QC procedures is provided in ISO 14385-1 and ISO 14385-2.

8.2 Sampling

8.2.1 Sampling location

The sampling site shall be in an accessible location where a representative measurement can be made. In addition, the sampling location shall be chosen with regard to safety of the personnel.

8.2.2 Representative sampling

It is necessary to ensure that the gas concentrations measured are representative of the average conditions inside the flue gas duct.

NOTE The selection of sampling points for representative sampling is described e.g. in ISO 10396, where gas stratification, fluctuations in gas velocity, temperature and others are mentioned.

8.3 Calculation

8.3.1 Conversion from volume to mass concentration for CO

Results of the measurement for CO shall be expressed as mass concentrations at reference conditions.

If the CO concentration is provided as a volume fraction, [Formula \(1\)](#) shall be used to convert volume fraction of CO (10^{-6}), ϕ_{CO} , to CO mass concentrations, γ_{CO} :

$$\gamma_{\text{CO}} = \phi_{\text{CO}} \cdot M_{\text{CO}} / V_M \quad (1)$$

where

- γ_{CO} is the CO mass concentration in mg/m³;
- φ_{CO} is the volume fraction of CO (by volume, 10⁻⁶);
- M_{CO} is the molar mass of CO (=28,010 g/mol);
- V_M is the molar volume (= 22,4 l/mol at standard conditions).

8.3.2 Conversion from wet to dry conditions for CO, CO₂ and O₂ concentrations

The CO concentration measured in the wet gas shall be corrected to the CO concentration at standard conditions, using [Formula \(2\)](#):

$$\gamma_s = \gamma_{\text{CO}} \cdot \frac{T}{273,15} \cdot \frac{101,325}{101,325 + p} \quad (2)$$

where

- γ_{CO} is the CO mass concentration measured in the wet gas (mg/m³);
- γ_s is the CO mass concentration in the wet gas at standard conditions in mg/m³ (273,15 K; 101,325 kPa);
- T is the temperature (K);
- p is the difference between the static pressure of the sample gas and the standard pressure (kPa).

If necessary, the CO concentration measured in the wet gas should be corrected to the CO concentration at reference conditions (dry gas), using [Formula \(3\)](#):

$$\gamma_r = \gamma_{\text{CO}} \cdot \frac{T}{273,15} \cdot \frac{101,325}{101,325 + p} \cdot \frac{100 \%}{100 \% - h} \quad (3)$$

where

- γ_{CO} is the CO mass concentration measured in the wet gas (mg/m³);
- γ_r is the CO mass concentration at reference conditions in mg/m³ (273,15 K; 101,325 kPa; H₂O corrected);
- T is the temperature (K);
- p is the difference between the static pressure of the sample gas and the standard pressure (kPa);
- h is the absolute water vapour content (volume fraction) (%).

The concentration of CO₂ or O₂ measured in the wet gas can be corrected to the CO₂ or O₂ concentration at reference conditions (dry gas), by using the [Formula \(3\)](#) by substituting CO₂ or O₂ for γ_{CO} .

9 Quality assurance and quality control procedures

9.1 General

Quality assurance and quality control (QA/QC) are important in order to ensure that the uncertainty of the measured values for CO, CO₂ and O₂ is kept within the limits specified for the measurement task. The results of the QA/QC procedures shall be documented.

9.2 Frequency of checks

AMS shall be adjusted and checked after the installation and then during continuous operation. [Table 2](#) shows the minimum required test procedures and frequency of checks. The user shall implement the relevant procedures for determination of performance characteristics or procedures described in this paragraph and [Annex E](#). The results of the QA/QC procedures shall be documented.

Table 2 — Minimum checks and minimum frequency of checks for QA/QC during the operation

| Check | Minimum frequency for permanently installed AMS | Test procedure |
|--------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------|
| Response time | Once a year | E.2 |
| Standard deviation of repeatability at zero point | Once a year | E.3.2 |
| Standard deviation of repeatability at span point | Once a year | E.3.3 |
| Lack-of-fit | Once a year and after any major changes or repair to the AMS, which will influence the results obtained significantly | E.4 |
| Sampling system and leakage check | Once a year or after any major changes or repair to the sampling system | E.7 |
| Beam alignment (in situ AMS only) | Once a year | According to manufacturer's manual |
| Light intensity attenuation through cleanliness and dust load (in situ AMS only) | According to manufacturer's requirements | According to manufacturer's manual |
| Cleaning or changing of particulate filters at the sampling inlet and at the monitor inlet | The particulate filters shall be changed periodically depending on the dust load at the sampling site. During this filter change the filter housing shall be cleaned. | According to manufacturer's manual |
| Zero drift ^a | Once in the period of unattended operation or period specified by national standards | E.8 |
| Span drift ^a | Once in the period of unattended operation or period specified by national standards | E.8 |
| Regular maintenance of the analyser | According to manufacturer's requirements | According to manufacturer's manual |

^a Analysers can be checked with internal gas cells or optical filters for this determination.

The user shall implement a procedure to guarantee that the reference materials used meet the uncertainty requirement specified in [Annex E](#), e.g. by comparison with a reference gas of higher quality.

9.3 Calibration, validation and measurement uncertainty

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

Permanently installed AMS for continuous monitoring shall be calibrated by comparison with

- a) an independent method of measurement, or
- b) a certified reference material.

In either case, the validation shall include the determination of uncertainty of the measured value obtained by calibrating the AMS. The AMS shall be subject to adjustments and functional tests according

to 9.2 before each calibration. This ensures that the measurement uncertainty is representative of the application at the specific plant.

The validation shall include the determination of the uncertainty of measured values obtained by comparison between reference gas or reference material with the AMS.

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, e.g. in ISO 20988.

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

10 Test report

It is presupposed that the test report satisfies applicable legal requirements. If not specified otherwise, it shall include at least the following information:

- a) a reference to this document, e.g. ISO 12039:2019;
- b) a description of the measurement objective;
- c) the 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, listed in [Table 1](#);
- f) operating range;
- g) sample gas temperature, sample gas pressure and optical path length through an optical cell (it is needed for only in situ measurement);
- h) details of the quality and the concentration of the span gases used;
- i) description of plant and process;
- j) the identification of the sampling plane;
- k) the actions taken to achieve representative samples;
- l) a description of the location of the sampling point(s) in the sampling plane;
- m) a description of the operating conditions of the plant process;
- n) the changes in the plant operations during sampling;
- o) the sampling date, time, and duration;
- p) the time averaging on relevant periods;
- q) the measured values;
- r) the measurement uncertainty;
- s) the results of any checks;
- t) any deviations from this document.

Annex A (informative)

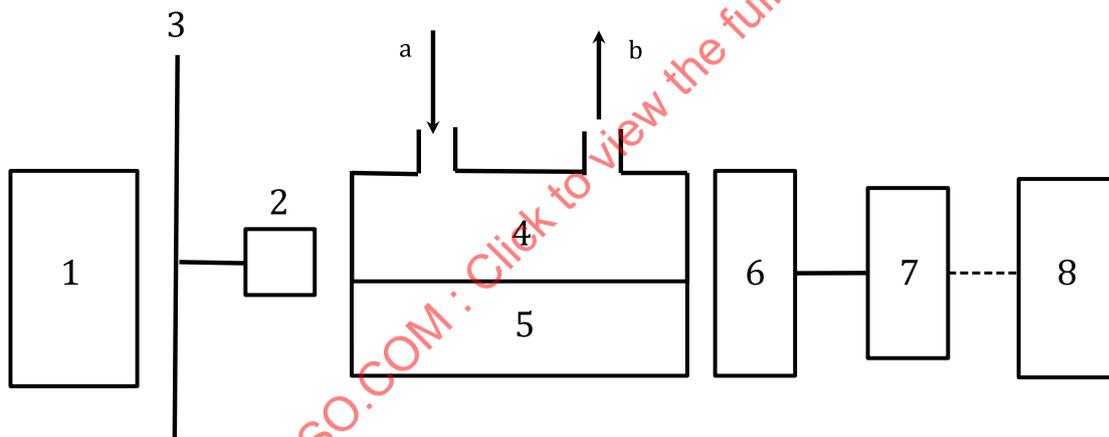
Infrared absorption method (CO and CO₂)

A.1 Measuring principle based on infrared absorption technique

The non-dispersive infrared absorption method is based on the principle that gases consisting of molecules with different atoms absorb infrared radiation at a unique wavelength. The measurement technique makes use of the principle as follows:

a) Dual beam method

The radiation emitted from an IR source is divided into two beams and then modulated, one beam passing through the measuring cell and the other through the reference cell containing an IR inactive gas, usually nitrogen. If the sample gas contains CO or CO₂, some of the IR energy is absorbed and the difference in IR energy reaching the detector is proportional to the amount of CO or CO₂ present. The detector is designed so that it is only sensitive to the CO or CO₂-specific wavelengths.



Key

- | | |
|------------------|---------------------|
| 1 IR source | 6 detector |
| 2 chopper motor | 7 electronics |
| 3 chopper wheel | 8 display |
| 4 sample cell | a Sample gas inlet. |
| 5 reference cell | b Gas outlet. |

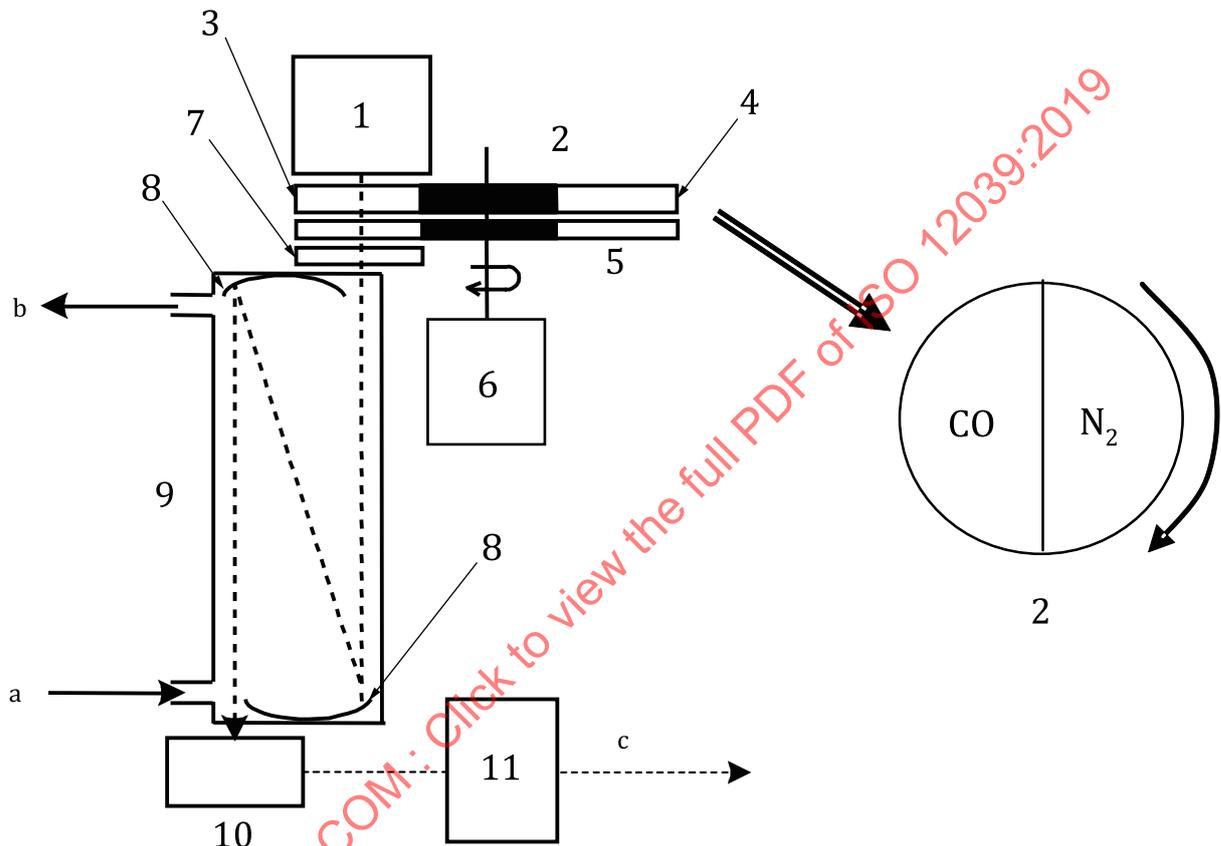
Figure A.1 — Diagram of a dual-beam type NDIR analyser

b) Single beam method

There are at least three types of single beam methods:

- Use of interference filters, with one filter at the absorption band for the gas being measured and the other filter at the reference wavelength. The gas concentration is then a function of the ratio of the measured and reference wavelengths. A tuneable filter with varying band pass wavelength may be employed instead of multiple filters.

- In the gas filter correlation (GFC) method the measurement interference filter is replaced with a gas filter; otherwise the method is similar to above. The gas analyser consists of the gas correlation filters, which are composed of the sample gas filter filled with the sample gas including CO or CO₂ and the reference gas filter filled with the correlation zero gas (N₂), and the chopper wheel. After the introduction of the sample gas into the sample cell, the gas correlation filters and the chopper wheel are rotated constantly. The gas analyser measures the differential IR absorption of a beam which alternatively passes through the sample gas filter and the reference gas filter. This gives better sensitivity and reduction of cross-sensitivity effects. Additional gas filters can be used to minimize the effect of interfering gases.

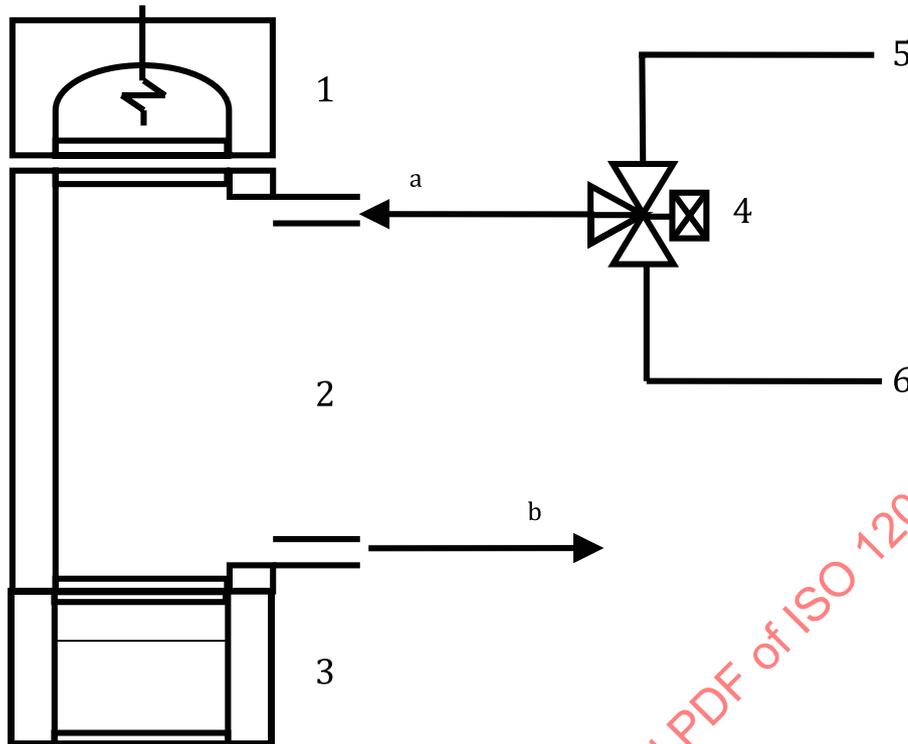


Key

| | | | |
|---|------------------------|----|-------------------|
| 1 | IR source | 8 | mirror |
| 2 | gas correlation filter | 9 | sample cell |
| 3 | sample gas filter | 10 | detector |
| 4 | reference gas filter | 11 | amplifier |
| 5 | chopper wheel | a | Sample gas inlet. |
| 6 | motor | b | Gas outlet. |
| 7 | optical filter | c | Output signals. |

Figure A.2 — Diagram of gas filter correlation type NDIR analyser

- Cross-modulation type non-dispersive infrared analyser detects the difference of infrared absorption caused by alternatively introducing the sample gas and the gas for reference (e.g., air with NO_x, SO₂ etc., removed) to the measurement cell. The difference measured is the level due to the measurand and in this way the effect of interfering components are removed.



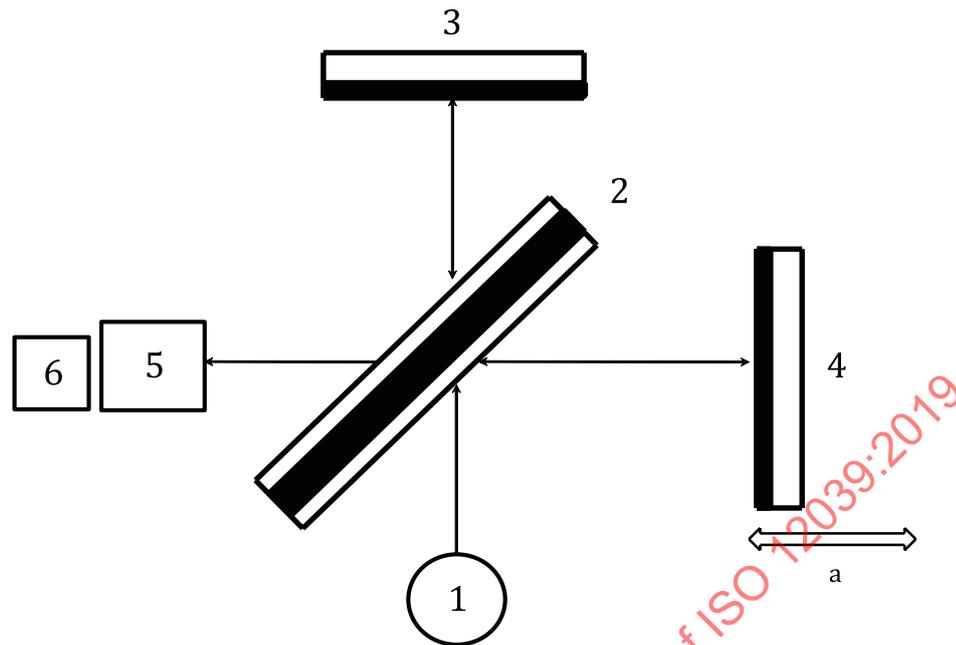
Key

- 1 IR source
- 2 sample cell
- 3 part for detection (optical filter and detector)
- 4 solenoid valve
- 5 sample gas
- 6 gas for reference
- a Gas inlet.
- b Gas outlet.

Figure A.3 — Diagram of cross-modulation type NDIR analyser

c) Fourier transform infrared spectroscopy

In a two-beam interferometer typically used for FTIR, the light emitted from infrared source is collimated and directed to a beam splitter. Part of the light passes through the beam splitter to a mirror, and the rest of the light is reflected to another mirror. Depending on the interferometer design, one or more mirrors are made to move, and as a result the beams will have travelled over different distances. When the two beams are reflected back to the beam splitter, there will be a phase difference between them. The combined output beam exiting the interferometer will have varying intensity as a function of the optical path difference (mirror position). This varying intensity signal is called the interferogram and it is linked to the wavelength spectrum by the Fourier Transformation. The spectrum is obtained in an FTIR instrument by recording the interferogram, applying some digital signal processing to it (apodization, filtering, phase correction) and computing its inverse Fourier transformation. The spectrum obtained is evaluated against established library spectra to derive the concentration of the gaseous species of interest (CO or CO₂).

**Key**

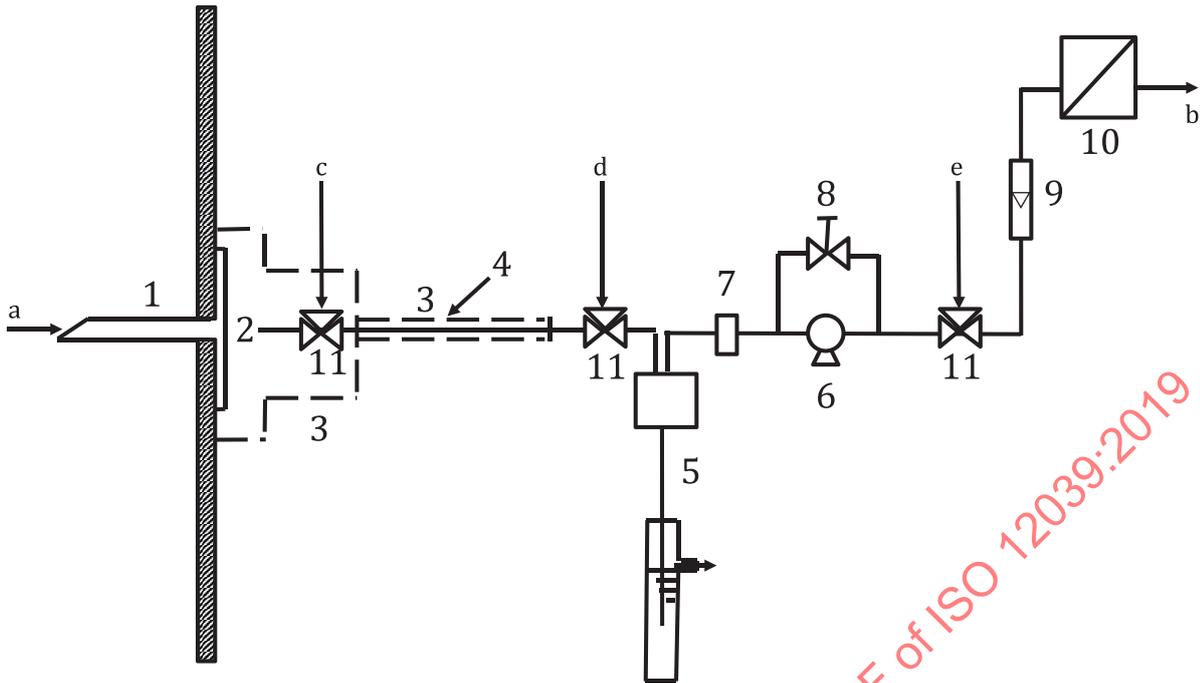
- 1 IR source
- 2 beam splitter (half-silvered mirror)
- 3 fixed mirror
- 4 moving mirror
- 5 sample cell
- 6 detector
- ^a Moving.

Figure A.4 — Diagram of Fourier transform infrared analyser

A.2 Description of the automated measuring system

A.2.1 Cold-dry extractive system

A representative volume of flue gas is extracted from the emission source at a controlled flow rate. Dust present in the volume sampled is removed by filtration before the sample gas is conditioned and passes to the analytical instrument. [Figure A.5](#) shows an arrangement of a complete measuring system with different possibilities for implementation.



Key

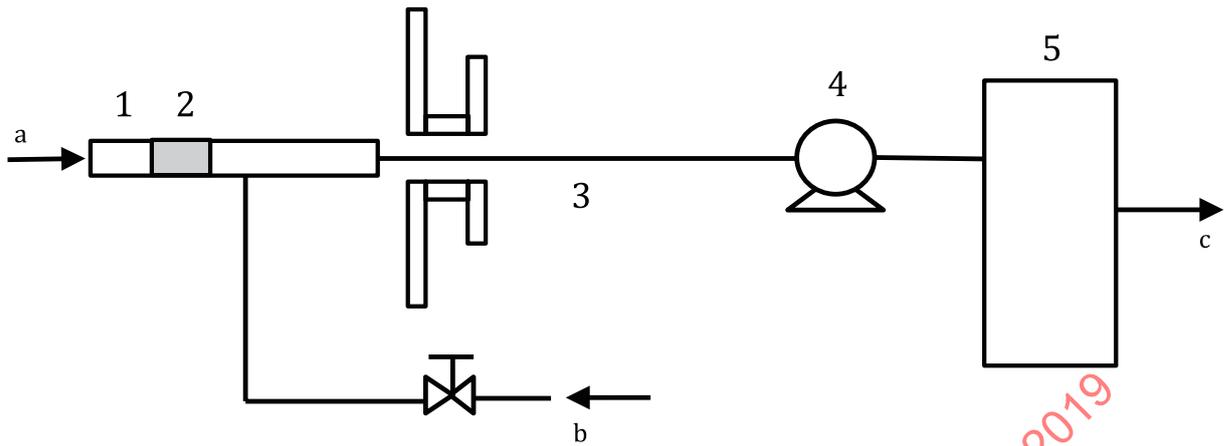
- | | |
|-------------------------------------------|-------------------------------------------------------------------------------------------------|
| 1 gas sampling probe | 9 flow meter |
| 2 primary filter | 10 analyser |
| 3 heating (for use as necessary) | 11 valve |
| 4 sampling line (heated as necessary) | a Sample gas inlet. |
| 5 sample cooler with condensate separator | b Gas output. |
| 6 sampling pump | c Inlet for zero and span gas (preferably in front of the nozzle) to check the complete system. |
| 7 secondary filter | d Inlet for zero and span gas to check the conditioning system and the analyser. |
| 8 needle valve | e Inlet for zero and span gas to check the analyser. |

EXAMPLE Cold-dry extractive type.

Figure A.5 — Diagram of the automated measuring system

A.2.2 Hot-wet extractive system

When analysers with a hot sample cell (for FTIR, NDIR and others) are used, the automated measuring system as shown in [Figure A.6](#) is often applied.

**Key**

- 1 sampling probe, heated (if necessary)
- 2 particle filter (in-stack or out-stack)
- 3 heated sampling line
- 4 sampling pump, heated
- 5 analyser with heated sample cell
- a Sample gas inlet.
- b Zero and span gas inlet.
- c Gas outlet.

EXAMPLE Hot-wet type.

Figure A.6 — Diagram of the hot optical measuring system

A.3 Components of the sampling and the sample gas conditioning systems

A.3.1 Sampling probe

The sampling probe shall be made of suitable, corrosion-resistant material (e.g. stainless steel, borosilicate glass, ceramic; PTFE is only suitable for flue gas temperature lower than 200 °C).

A.3.2 Filter

The filter is needed to remove the particulate matter, in order to protect the sampling system and the analyser. The filter shall be made of ceramic, PTFE, borosilicate glass or sintered metal. The filter shall be heated above the water or acid dew-point. A filter that retains particles greater than 2 µm is recommended. The size of the filter shall be determined from the sample flow required and the manufacturer's data on the flow rate per unit area.

The temperature of the sampling probe and the filter must be higher by at least 10 °C to 20 °C than the water or acid dew-point of the gases.

A.3.3 Sampling line

The sampling line shall be made of PTFE, PFA or stainless steel. The lines shall be operated at 15 °C above the dew-point of condensable substances (generally the water or acid dew-point). The tube diameter should be appropriately sized to provide a flow rate that meets the requirements of the analysers, under selected line length and the degree of pressure drop in the line as well as the performance of the sampling pump used.

A.3.4 Moisture removal system

The moisture removal system shall be used to separate water vapour from the flue gas. The dew point shall be sufficiently below the ambient temperature. Dew point of 2 °C to 5 °C is suggested. Sufficient cooling is required for the volume of gas being sampled and the amount of water vapour that it contains.

For the hot-wet extractive system ([A.2.2](#)), this moisture removal system is not used.

A.3.5 Sampling pump

A sampling pump is used to withdraw a continuous sample from the duct through the sampling system. This may be a diaphragm pump, a metal bellows pump, an ejector pump or other types of pumps. The pump shall be constructed of corrosion-resistant material. The performance of the pump shall be such that it can supply the analyser with the gas flow required. In order to reduce the transport time in the sampling line and the risk of physicochemical transformation of the sample, the gas flow can be greater than that required for the analytical units.

For the hot-wet extractive system ([A.2.2](#)), the pump shall be operated at a minimum of 180 °C.

A.3.6 Secondary filter

The secondary filter is needed to remove the remaining particulate material, in order to protect the pump and the analyser. A filter that retains particles greater than 1 µm is recommended. Acceptable materials are PTFE, borosilicate glass or sintered metals. The size of the filter shall be determined from the sample flow required and the manufacturer's data on the flow rate per unit area.

A.3.7 Flow controller and flow meter

The flow controller and flow meter are used to set the required flow. They shall be constructed of corrosion resistant material.

Annex B (informative)

Extractive O₂ measurement techniques

B.1 Measuring principle based on the paramagnetic, zirconium oxide and electrochemical cell methods

B.1.1 Paramagnetic method (O₂)

Oxygen is strongly paramagnetic and is attracted into a magnetic field. All other gases, with few exceptions, are either weakly paramagnetic or diamagnetic. This property can be used to make an analysis which is specific to oxygen.

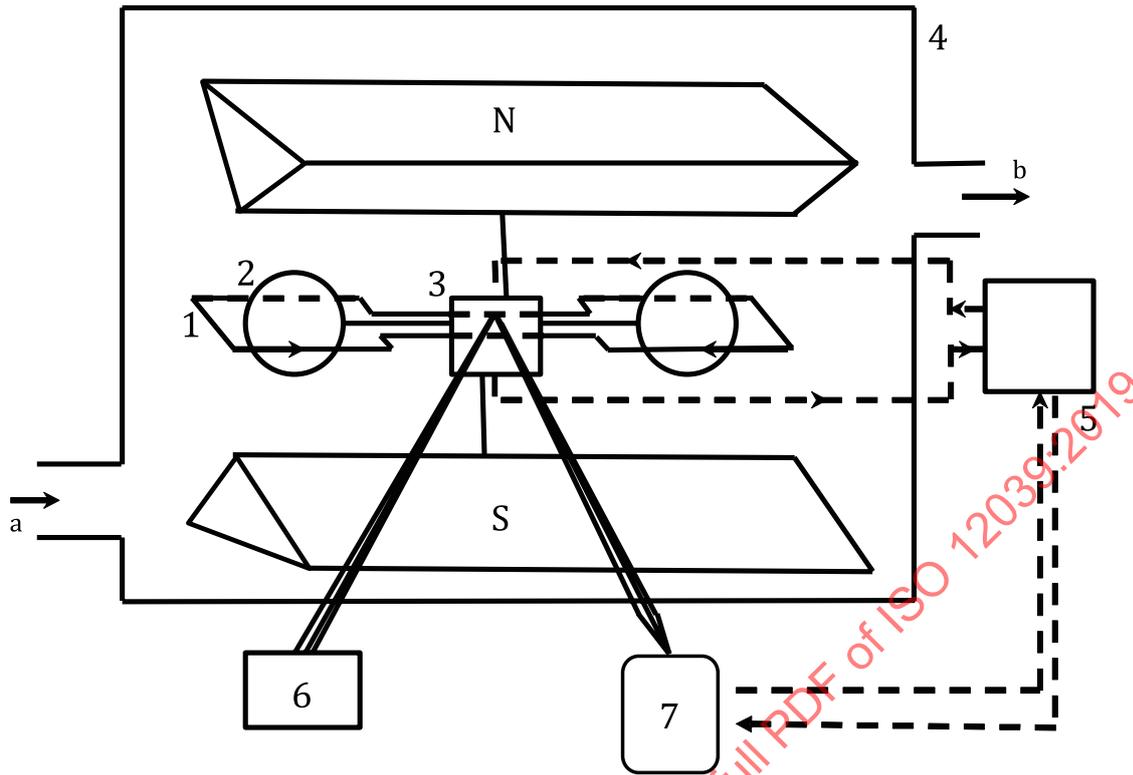
Three basic detection techniques are given as example here.

a) **Dumb-bell type analyser** (see Reference [Z])

An element, usually a torsion balance, forming a dumb-bell with diamagnetic glass spheres, is suspended in a strong, inhomogeneous magnetic field. The dumb-bell spheres are pushed away from the most intense part of the magnetic field. When the gas surrounding the dumb-bells contains oxygen, the spheres are pushed farther out of the field due to the change in the field caused by the paramagnetic oxygen.

The system is first set up without sample gas so that light will reflect off of a small mirror onto a photocell. In a feedback loop, a current is sent through a platinum wire that encircles the dumb-bell, creating an electromagnetic counter torque. This torque restores the mirror position so that the photocell will again detect the reflected light. The amount of restoration necessary (current through the wire) when oxygen is present is related to the oxygen concentration.

A schematic diagram of a typical configuration of a dumb-bell type analyser is shown in [Figure B.1](#).



Key

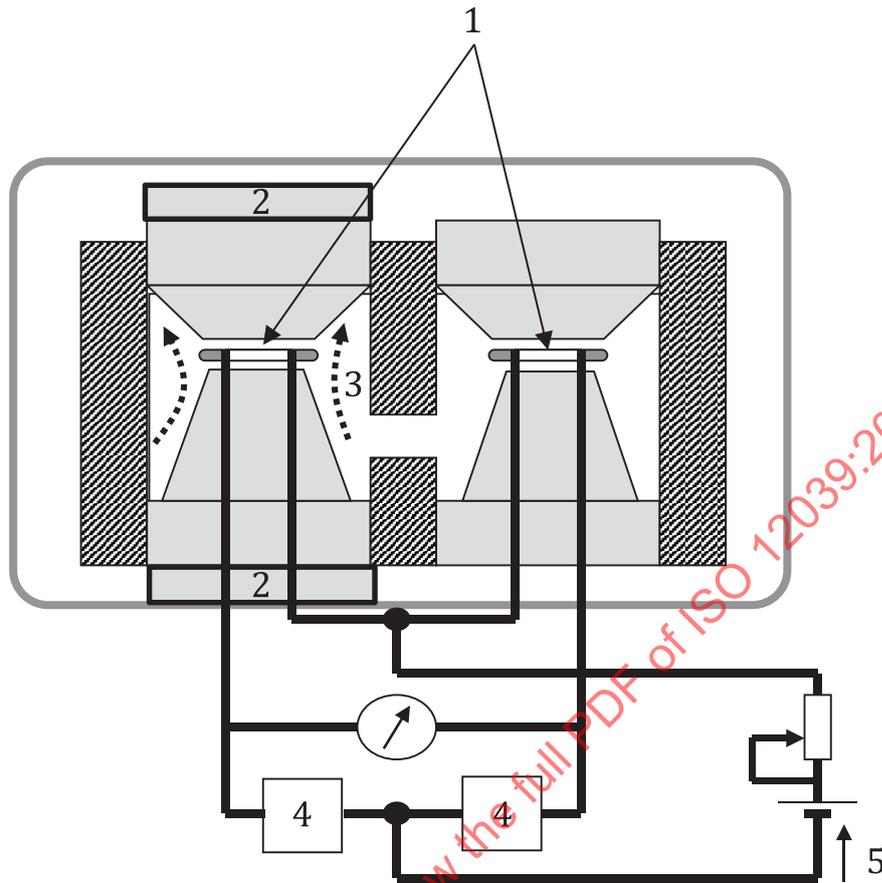
- | | | | |
|---|------------------|---|----------------------|
| 1 | feedback coil | 5 | feedback circuit |
| 2 | dumb-bell | 6 | lamp |
| 3 | mirror | 7 | photocell (detector) |
| 4 | measurement cell | a | Sample gas inlet. |
| | | b | Sample gas outlet. |

Figure B.1 — Diagram of a paramagnetic method (Dumb-bell type)

b) Magnetic wind type analyser

A second technique uses the temperature coefficient of the paramagnetic effect. The paramagnetic coefficient is inversely proportional to the absolute temperature. If a strong magnetic field is combined with a temperature gradient, then a flow of oxygen gas will be created. The rate of flow (magnetic wind) is a function of oxygen concentration and can be measured, for example by thermal conductivity techniques.

A schematic diagram of a typical configuration of magnetic wind type analyser is shown in [Figure B.2](#).

**Key**

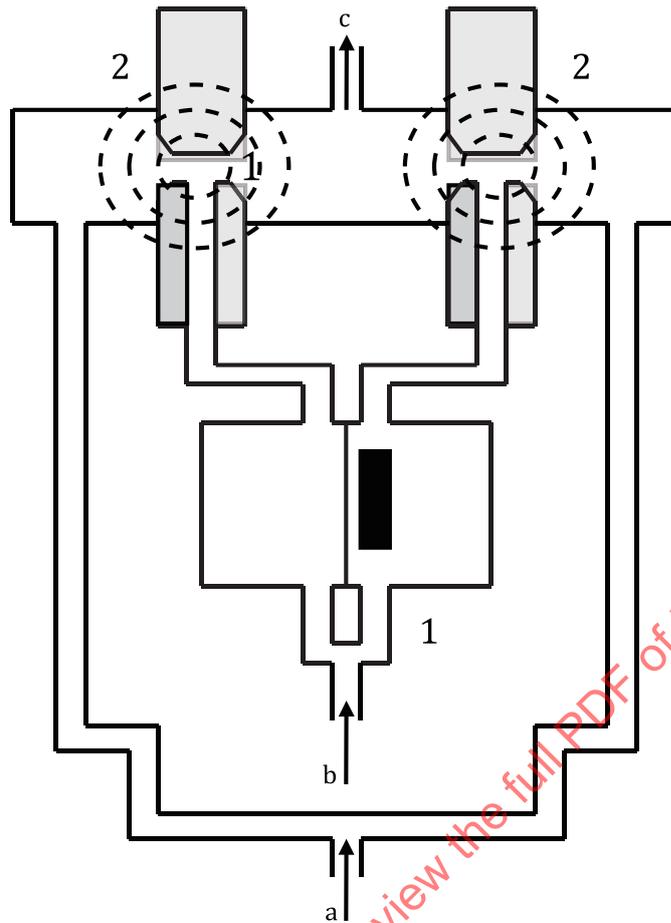
- 1 heating filament
- 2 magnet
- 3 magnetic wind
- 4 resistor
- 5 bridge current

Figure B.2 — Diagram of a paramagnetic method (Magnetic wind type)

c) Magneto pneumatic type analyser

The third technique utilizes a strong magnetic field across a tube. If oxygen, which is paramagnetic gas is in an uneven magnetic field, it is attracted to the stronger portion of the magnetic field increasing the pressure in that portion. The pressure increase at this time is taken out from the magnetic field using a carrier gas (N_2). It is detected by like a capacitor diaphragm/microphone detector.

A schematic diagram of a typical configuration of a magneto pneumatic type analyser is shown in [Figure B.3](#).



- Key**
- 1 detector
 - 2 electromagnet
 - a Sample gas.
 - b Carrier gas.
 - c Gas outlet.

Figure B.3 — Diagram of a paramagnetic method (Magneto pneumatic type)

B.1.2 Zirconium oxide method (O₂)

The zirconium oxide (ZrO₂) method measures the oxygen in a flue gas using an yttria-stabilized zirconium oxide cell with porous platinum electrodes coated on both its inner and outer surfaces. When this cell is heated to a high temperature, above 600 °C, it becomes permeable to oxygen ions. Vacancies in its crystal lattice permit the mobility of oxygen ions so that the cell becomes an oxygen-ion-conducting solid electrolyte.

The platinum electrodes on each side of the cell provide a catalytic surface for the change of oxygen molecules to oxygen ions and oxygen ions to oxygen molecules. Oxygen molecules of the high-concentration gas side of the cell gain electrons to become ions that enter the electrolyte. Simultaneously, at the other electrode, oxygen ions lose electrons and are released from surface of the electrode as oxygen molecules.

When the concentration of oxygen is different on each side of the cell, oxygen ions migrate from the high oxygen concentration side to the low oxygen-concentration side. This ion flow creates an electronic imbalance that results in a voltage potential between the electrodes which is a function of the temperature of the cell and the ratio of oxygen partial pressure on each side of the cell.

The output voltage as a function of temperature and oxygen concentrations in the sample and reference gases is given by the Nernst equation:

$$E = \left[\frac{RT}{4F} \right] \ln \frac{p_1}{p_2}$$

where

E is the output voltage;

R is the gas constant;

T is the absolute temperature;

F is the Faraday constant;

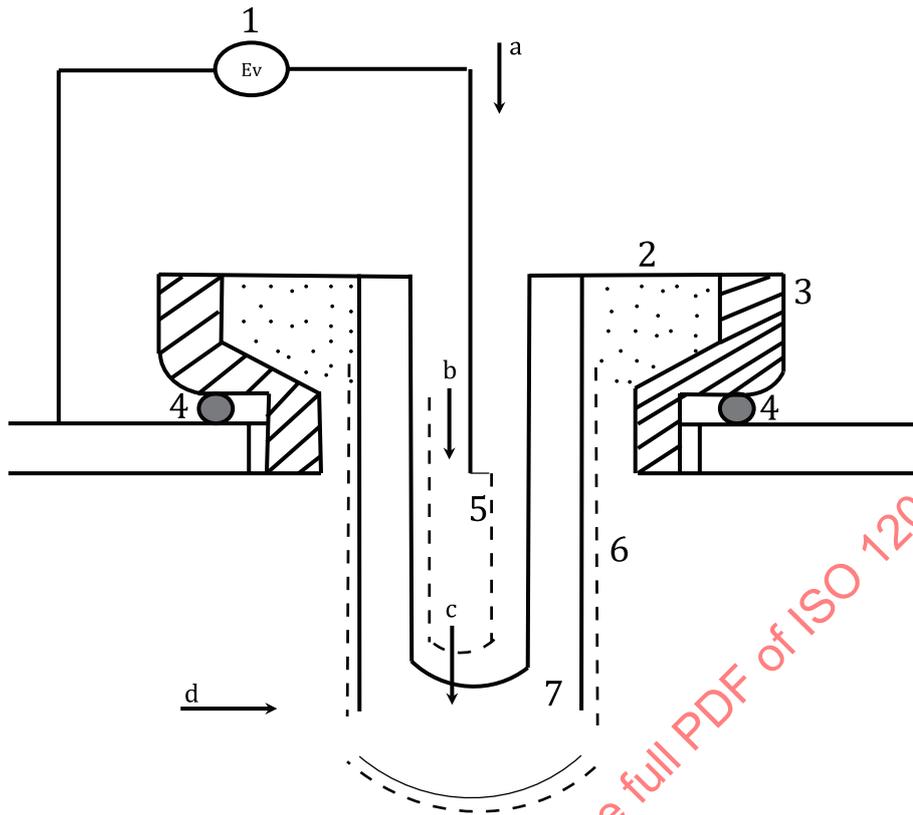
p_1 is the partial pressure of O_2 in the gas for reference;

p_2 is the partial pressure of O_2 in the process gas.

NOTE In practice, certain zirconium cells may not exactly follow the Nernst equation.

A schematic diagram of a typical configuration of a ZrO_2 type analyser (see Reference [8]) is shown in [Figure B.4](#).

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Key

- | | | | |
|---|---------------------------------|---|-------------------------------|
| 1 | electric signal | 6 | outer Pt. electrode |
| 2 | electrically conductive sealing | 7 | ZrO ₂ -electrolyte |
| 3 | metal mounting | a | Air O ₂ . |
| 4 | sealing | b | Reference gas "air". |
| 5 | inner Pt. electrode | c | O ₂ . |
| | | d | Exhaust gas. |

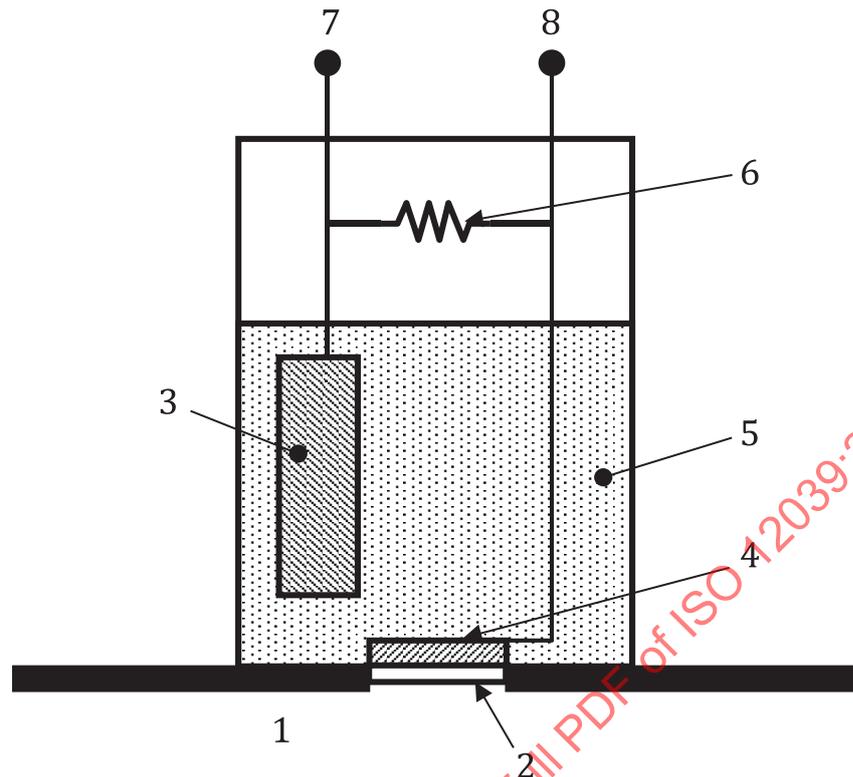
Figure B.4 — Diagram of a zirconium oxide method

B.1.3 Extractive electrochemical cell method (O₂)

Electrochemical cells can be used to measure O₂ if the electro-oxidation or electro-reduction of the gas molecules at an electrode results in a current that is directly proportional to the partial pressure of the gas. In these cells, the gas diffuses through a selective semipermeable membrane to an electrode and electrolytic solution. The gas reacts at the electrode and a product of the reaction is transported to a counter-electrode where it, in turn, reacts.

The current generated from the difference in electromotive force (emf) from the cathode/anode reactions is measured. A retarding potential can be maintained across the electrodes to prevent the oxidation of gas species that might otherwise interfere.

A schematic diagram of a typical configuration of an electrochemical analyser is shown in Figure B.5.

**Key**

- | | | | |
|---|--------------------|---|-------------|
| 1 | sample gas | 5 | electrolyte |
| 2 | diaphragm | 6 | resistor |
| 3 | negative electrode | 7 | anode |
| 4 | positive electrode | 8 | cathode |

Figure B.5 — Diagram of electrochemical cell method

B.2 Description of the automated measuring system

A representative volume of flue gas is extracted from the emission source at a controlled flow rate. Particulate matter present in the volume sampled is removed by filtration before the sample passes to the analytical instrument. A typical arrangement of a complete measuring system for O₂ is same as that described in [A.2.1](#) (CO and CO₂ based on NDIR).

ZrO₂ sensor can also be used in hot wet extractive systems (described in [A.2.2](#)) or in situ measuring system.

Annex C (informative)

In situ CO, CO₂ and O₂ measurement

C.1 Measuring principle based on in situ CO, CO₂ and O₂ measurement with Tuneable Laser Spectroscopy (TLS) technique

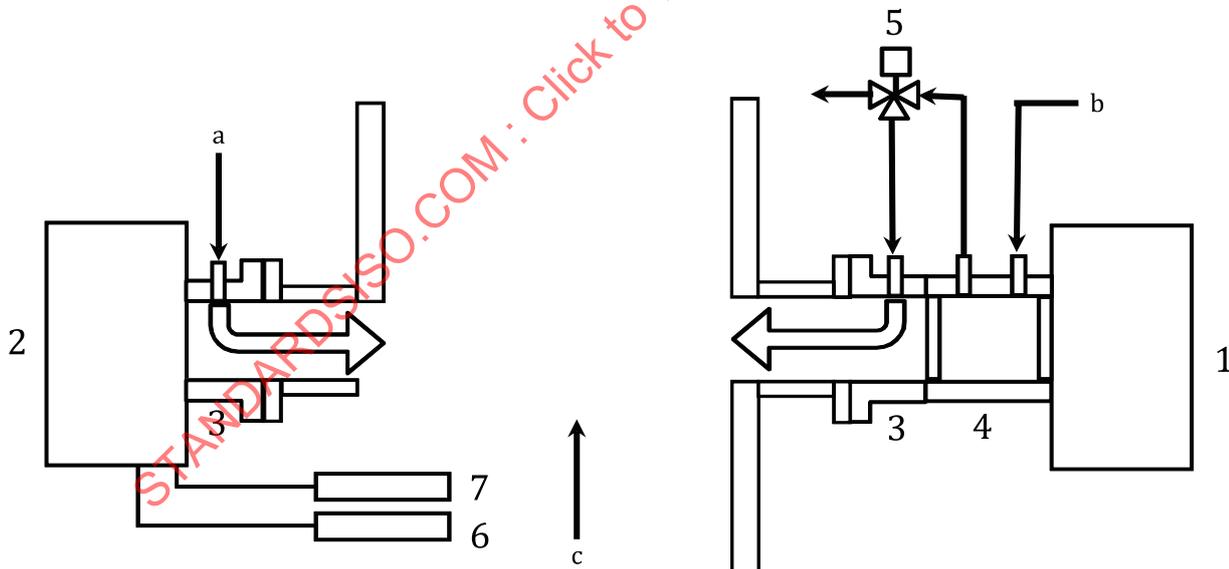
An example of an in situ TLS is shown below however extractive systems are also available. The analysis principle is based upon measurement of unconditioned CO, CO₂ and O₂ in the stream. CO, CO₂ and O₂ levels are determined by direct measurement with a tuneable laser analyser. For the correction to dry standard conditions it is recommended to measure water vapour together with the CO, CO₂ or O₂ concentration.

NOTE Analysers based on NDIR and FTIR principles are also offered for in situ measurements.

C.2 In situ cross duct measuring systems

C.2.1 General

The in situ TLS measuring system consists of a transmitter and receiver unit. The two units are mounted opposite each other directly on the pipe or stack. [Figure C.1](#) shows a typical arrangement of an in situ measuring system based on tuneable laser for CO, CO₂ or O₂



Key

- | | |
|--------------------|--------------------------------------------------------------------------------|
| 1 transmitter unit | 6 pressure sensor (if the duct has constant conditions, it is not required) |
| 2 receiver unit | 7 temperature sensor (if the duct has constant conditions, it is not required) |
| 3 purging flanges | a Purge gas. |
| 4 validation cell | b Purge gas, span gas or zero gas. |
| 5 three-way valve | c Stack gas region. |

Figure C.1 — Diagram of an in situ TLS measuring system (example)

C.2.2 Components of an in situ TLS measuring system (cross duct)

C.2.2.1 Transmitter and receiver unit

The transmitter unit contains a laser light source and the receiver unit contains a photo detector. The light beam is emitted from laser diode located in the transmitter unit. The laser light passes through the gas and strikes the photo detector in the receiver unit.

C.2.2.2 Optical window purge

The purging flanges have two functions. First, the flanges are used to mount the transmitter or receiver unit on the pipe. Second, the purging flange has a connection port for the purging.

If required by the application, purge gas is applied to keep the windows clean in order to prevent the contamination of the optical components by the flue gas. The purge medium enters the purging flange and flows in the direction of the duct, where it is mixed with the flue gas. As purge medium usually instrument air is used. The purge flow depends on the conditions and is typically between 20 l/min and 50 l/min.

C.2.2.3 Validation cell [CO only]

To verify the functionality of the TLS measuring system, a validation procedure can be conducted regularly.

One method for validation is to apply an external validation cell, which is permanently mounted in the optical path between the pipe and the transmitter/receiver unit. An alternative method is to use a gas filled cell with stable concentration.

During the validation procedure, the validation cell is flushed with certified test gas or gas filled validation cell is temporarily moved into the optical path respectively.

The gas concentration required for both methods depends on the optical path length and validation cell, as well as the measuring range. Typically test gas with a concentration equivalent to 70 % to 90 % of full span is used.

NOTE Calculated O₂ and CO₂ concentrations in the validation cell can exceed 100 % making the procedure unsuitable.

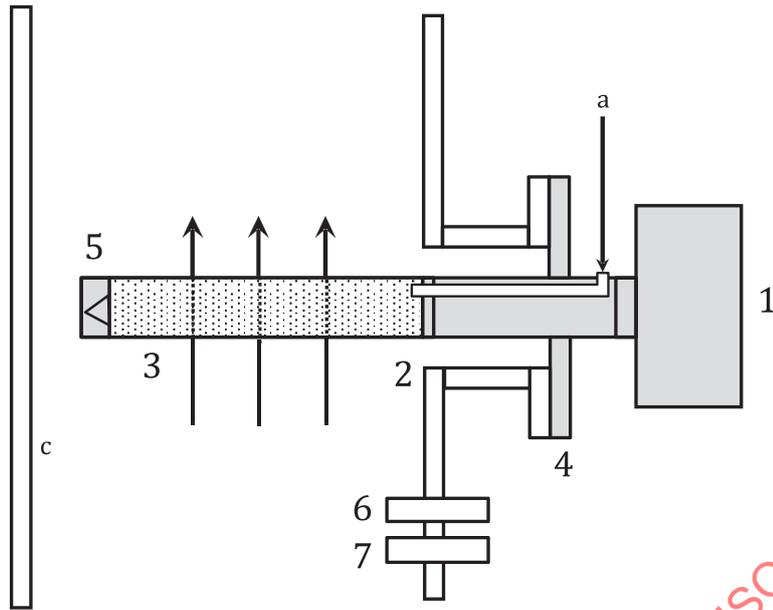
C.2.2.4 Pressure and temperature sensor

Due to the in situ installation, varying gas pressures and gas temperatures in flue gas may have an effect on the measurement signal. If the parameters exceed the maximum acceptable variations, pressure and/or temperature sensors can be applied to provide the relevant gas pressure or temperature to the TLS measuring system to correct for the influence of temperature and pressure variations.

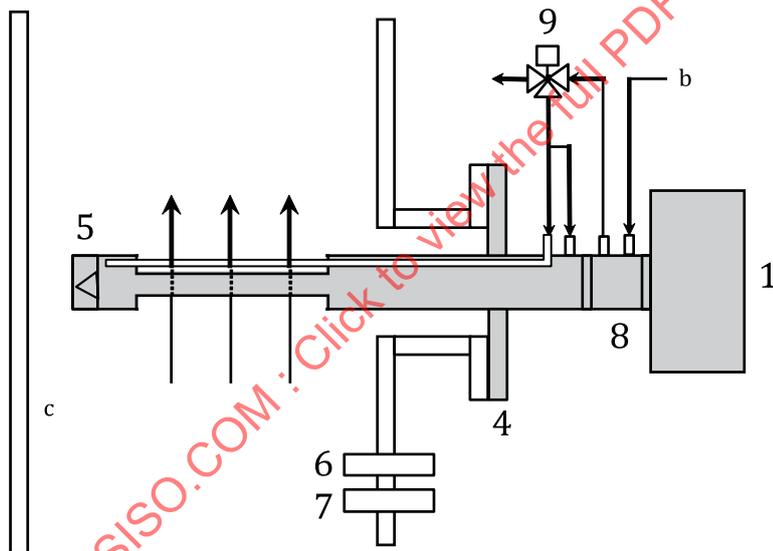
C.3 In situ point measuring systems

C.3.1 General

The in situ point measuring system consists of a transceiver unit and a probe. The beam is typically transmitted through a short path of sample gas stream and reflected by the mirror at the tip of the probe. [Figure C.2](#) shows a typical arrangement of an in situ point measuring system.



a) Filter type (a side view of the probe)



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b) Non-Filter type(a side view of the probe)**Key**

- 1 transceiver unit
- 2 probe
- 3 probe filters
- 4 probe flange
- 5 mirror
- 6 pressure sensor (if the duct has constant conditions, it is not required)
- 7 temperature sensor (if the duct has constant conditions, it is not required)
- 8 validation cell
- 9 three-way valve
- a Span gas or zero gas.
- b Purge gas, span gas or zero gas.
- c Stack gas region.

Figure C.2 — Example of an in situ TLS measuring system (point monitor)**C.3.2 Components of an in situ TLS measuring system (point monitor)****C.3.2.1 General**

In situ point monitors sample the gas stream in the duct at the end of the probe. Gas is typically monitored over a short path, depending upon the principle of measurement (see [Figure C.2](#)).

C.3.2.2 Instrument transceiver

The component of the instrument sensing the response of the measurement cell and generate an electrical signal that corresponds to the concentration of the gas being measured.

C.3.2.3 Measurement cell

A cell or cavity exposed to the gas stream, for the purpose of producing an electro-optical response to the gas concentration at the end of the probe.

C.3.2.4 Probe filter

A porous ceramic or sintered metal tube or screen minimizes the interference of particulate matter with the gas measurement. If little effect of particulate matter on the measurement is expected, it is possible to use a non-filter probe.

Annex D (normative)

Operational gases

D.1 General

Several operational gases are required when using this document.

D.2 Zero gas

Zero gas shall not contain compounds which interfere with the measuring efficiency of the instruments. For all analysers, pure nitrogen (5,0 grade, with the impurity of components to be measured less than the analytical detection limit), purified ambient air or other mixtures of O_2 and N_2 shall be used, however, for ZrO_2 method the "air point" shall be used. With air as the sample gas, the ZrO_2 cell gives a zero output (but the analyser reads 21 % O_2) as a result ZrO_2 sensor usually uses a zero-gas surrogate at a concentration of 2 % or 3 % O_2 .

The concentration of the species of interest within the zero gas shall not exceed 1,0 % of the measuring range used.

D.3 Span gases

Span gas shall consist of CO or CO_2 in purified air or N_2 or O_2 in N_2 . 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 % to 90 % of the upper limit of the selected measuring range. The ZrO_2 cell may use other span gas concentrations, because of the measuring principle.

D.4 Reference gas

Reference gas shall consist of CO or CO_2 in purified air or O_2 in nitrogen. It shall have a known concentration with a maximum permissible expanded uncertainty of 2,0 % of its nominal value traceable to applicable standards.

Annex E (normative)

Procedures for determination of the performance characteristics

E.1 General

Before any tests are being 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 two hours should be taken.

Before determining the performance characteristics of an AMS, the instrument shall be set up according to the manufacturer's requirements and according to the procedure detailed in [9.3](#).

During the 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.

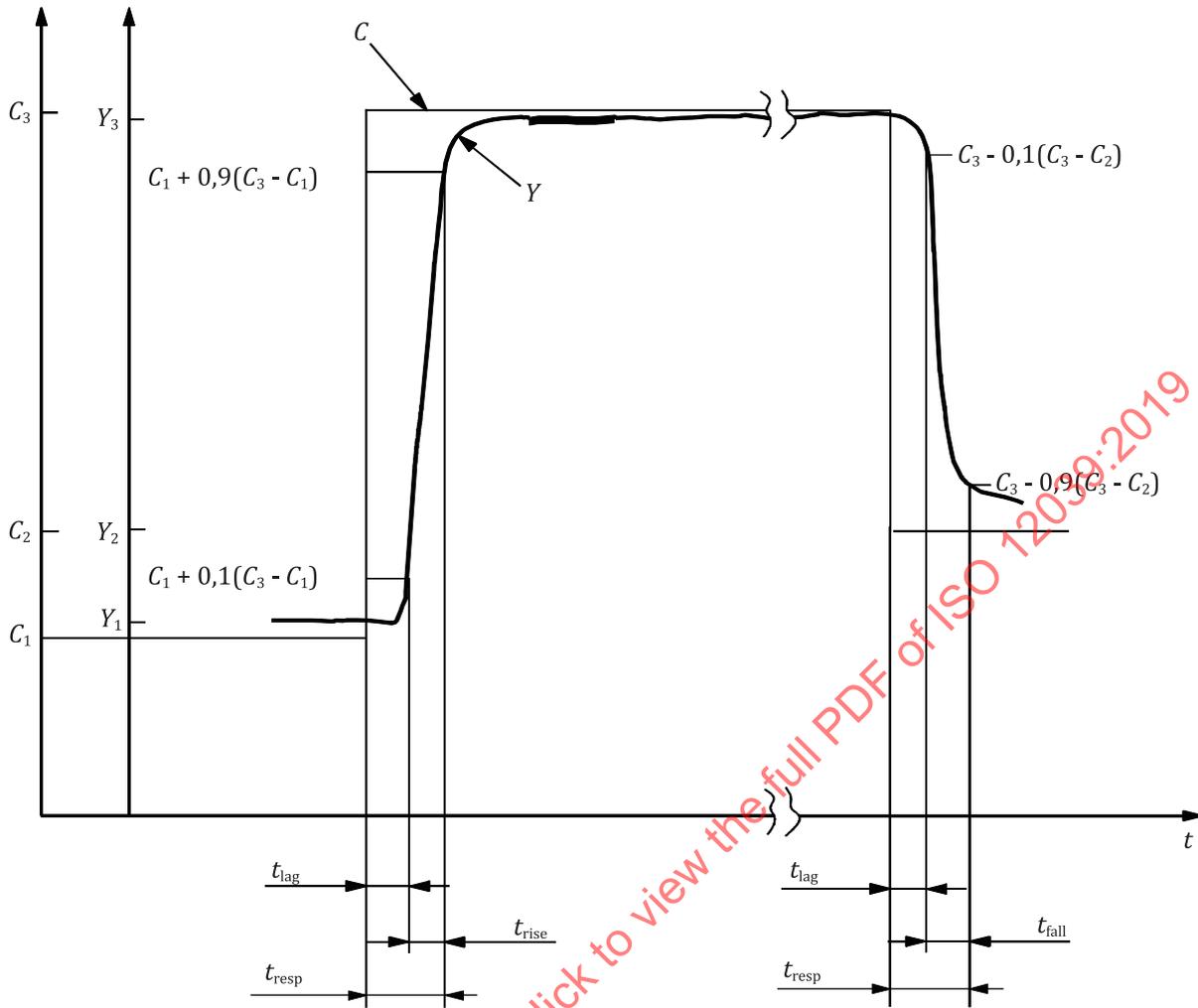
NOTE Response time, repeatability at zero and at span level, lack-of-fit, cross-sensitivity, zero drift and span drift, sensitivity to ambient temperature, sensitivity to electric voltage of in situ systems can be measured with an external test cell.

E.2 Response time

In order to establish response time, lag time, rise time and fall time, a step function of the measurand shall be input to the continuous automatic measuring system. Unless otherwise specified in the terms of reference, the step 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. The step change of the test facility shall correspond to at least 60 % of the measuring range (see [Figure E.1](#)). 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 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.

NOTE A significant difference between the rise time and the fall time indicates memory effects, i.e. dependence of a result of measurement on the values of the measurand during previous measurement(s).



Key

- t time
- C_i value of the measurand in reference material i
- Y_i output signal obtained by measuring the measurand in reference material i
- t_{lag} lag time
- t_{rise} rise time
- t_{fall} fall time
- t_{resp} response time

Figure E.1 — Illustration of the time characteristics of an automated measuring system; Change of the output signal Y (output) after a change of the reference value C (input) as a function of time t

E.3 Repeatability at zero and at span level

E.3.1 General

To determine repeatability at zero and at span level, several measurements are conducted at zero and at a span concentration according to the procedures in [E.3.2](#) and in [E.3.3](#). Standard deviation and repeatability are calculated for both series of measurement (zero and span value) according to ISO 9169.

E.3.2 Standard deviation of repeatability in laboratory 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 analyser. Then zero gas is to be applied to the sample inlet.

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 put in a zero gas or go back to flue gas and then measure span gas, at least 10 times.

The measured values obtained shall be used to determine the standard deviation of repeatability at zero point using [Formula \(E.1\)](#):

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

where

s_r is 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.

The standard deviation of repeatability at zero point shall meet the performance criterion specified in [Table 1](#).

NOTE Independent reading is the reading that is not influenced by a previous individual reading by separating two individual readings by at least four response times.

E.3.3 Standard deviation of repeatability in laboratory 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). The span gas has to be applied to the sample inlet. 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 the time equivalent to one independent reading and then put in a zero gas or go back to flue gas and then measure span gas, at least 10 times. The measured signals obtained shall be used to determine the standard deviation of repeatability at span using [Formula \(E.1\)](#).

The standard deviation of repeatability at span point shall meet the performance criterion specified in [Table 1](#).

E.4 Lack-of-fit (Linearity)

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 c_i at least 3 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. In this test procedure, a regression line is established between the instrument readings of the AMS (x values) and the test gas values (c 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, \dot{x}_i , estimated by the regression line is calculated according to [Formula \(E.2\)](#):

$$e_i = |\dot{x}_i - \bar{x}_i| \tag{E.2}$$

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.

E.5 Cross-sensitivity

The influence of potentially interfering substances also present in the flue gas shall be determined by admitting test gas mixtures to the input of the complete AMS (upstream of the test gas cooler, where present). The gas mixtures shall be produced with a mixing system in which an interferent is added to the gases for zero point and span point. The mixing system shall be compliant with national standards and shall have a maximum expanded uncertainty of 1 %. Reference materials (e.g. gases) shall be certified (traceable to national standards) and shall have an expanded uncertainty no greater than 2 %.

Interferents and their concentrations are defined in relation to the measuring principle and the intended measurement objective. The interferents listed in [Table E.1](#) shall be examined. The interferents shall be admitted individually.

Test gas without interferent and then with the interferent shall be applied. The measured signals of the AMS shall be determined for each test gas by waiting the time equivalent to one independent reading and then recording three consecutive individual readings. The three individual readings shall be averaged.

The deviations between the average reading with and the average reading without the interferent present at the zero point and span point shall be determined for each interferent.

All positive deviations above 0,5 % of the span gas concentration shall be summed and all negative deviations below -0,5 % of the span gas concentration shall be summed at both the zero point and span point. The maximum of the absolute values of the four summations shall meet the performance criteria specified in [Table 1](#).

The individual readings, averages and deviations at zero point and span point and for all interferents as well as the maximum deviation shall be reported.

Table E.1 — Concentrations of interferents used during cross sensitivity tests

| Interferent | Mass or volume concentration | |
|------------------|------------------------------|-------------------|
| | Value | Unit |
| O ₂ | 3 ^a and 21 | % |
| H ₂ O | 30 | % |
| CO | 300 | mg/m ³ |
| CO ₂ | 15 | % |
| CH ₄ | 50 | mg/m ³ |
| N ₂ O | 20 | mg/m ³ |

^a A test with 3 % oxygen concentration is used instead of a test without interferent.

Table E.1 (continued)

| Interferent | Mass or volume concentration | |
|--------------------------------------------------------------------------------------------------|------------------------------|-------------------|
| | Value | Unit |
| N ₂ O (fluidised-bed firing) | 100 | mg/m ³ |
| NO | 300 | mg/m ³ |
| NO ₂ | 30 | mg/m ³ |
| NH ₃ | 20 | mg/m ³ |
| SO ₂ | 200 | mg/m ³ |
| SO ₂ (coal-fired power stations without desulphurisation) | 1 000 | mg/m ³ |
| HCl | 50 | mg/m ³ |
| HCl (coal-fired power stations) | 200 | mg/m ³ |
| ^a A test with 3 % oxygen concentration is used instead of a test without interferent. | | |

E.6 Check of losses in the sampling line and conditioning system

The losses in the sampling line and conditioning system shall be checked by supplying zero gas and span gas to the analyser through the sampling system, as close as possible to the nozzle (in front of the filter if possible) and secondly direct to the analyser. The test gas should have a CO, CO₂ or O₂ concentration of about 70 % to 80 % of the measuring range. Possible impurities in the entire system may lead to memory effects due to adsorption or desorption to or from the surfaces. Differences shall be less than 2 %.

E.7 Check of leakage in the sampling line and conditioning system

The sampling system shall be checked for leaks. The procedure of leak test is as follows:

- assemble the complete sampling system, including charging the filter housing and absorbers;
- allow the sampler to warm up to its operating temperature;
- seal the nozzle inlet;
- close the nozzle and switch on the pump(s);
- after reaching minimum pressure read the flow rate.

E.8 Zero drift and span drift for performance test

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

The position of the zero point and of the span point shall be determined manually by applying 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](#).

E.9 Zero drift and span drift for periodical test

Instrument adjustments with zero and span gases or with other reference materials shall be carried out at least once in the period of unattended operation. Tests for instruments for periodical measurements shall be carried out at the beginning of each measurement series.

The zero and span gas or other reference materials shall be used under the same flow and pressure conditions as for measurement conditions. For zero and span gas the sample port of the instrument or a procedure according to the manufacturer's instructions should be used. 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](#).

E.10 Excursion of measurement beam of cross-stack in situ AMS

Gradually and precisely deflect the transmitter and receiver assemblies of the AMS in the horizontal and vertical planes, and then record the measured signals using reference materials.

NOTE 1 This test typically applies to cross-stack in situ optical techniques. The test also applies to extractive AMS with separate transmitter and receiver assemblies.

NOTE 2 This testing requires calibration standards (e.g. reference filters) and an optical bench.

NOTE 3 Typically the experimental path length for this test can be from 1 m up to 5 m at least, although the test should be performed at the maximum path length practical.

Deflections shall be carried out for both the position of the zero point and as well as for that of a span point for approx. 70 % to 90 % of the output range over two typical measurement path lengths. The deflection is to be performed in incremental steps of approximately 0,05° in the angle range demanded.

The range of deflection shall be equal to at least twice the angle specified by the manufacturer. It should also be tested as far as the deflection limit permitted by the assemblies — if necessary in larger increments.

The efficiency of any manual optical adjustment facilities shall be examined at least in qualitative terms. Automatic adjustment processes shall be activated and included in the test.

The measured signals obtained for the various test steps shall be included in tabular form in the test report. These measured signals shall be paired up with the deflection angles.

The maximum permissible deflection angles shall be stated within which the AMS satisfies the performance criterion. In the case of automatically aligning AMS, the manner of operation shall be described and verified by means of test results.

E.11 Sensitivity to sample gas pressure, for a pressure change of 2 kPa

Determine the influence of variations in sample gas pressure on the response of the AMS. The sample shall be nitrogen containing the measured component at a concentration of between 70 % and 80 % of the upper limit of the certification range.

Measure the output signal of the AMS when the sample gas pressure is at

- the ambient atmospheric pressure;
- approximately 2 kPa above ambient atmospheric pressure, within limits of $\pm 0,2$ kPa;
- approximately 2 kPa below ambient atmospheric pressure, within limits of $\pm 0,2$ kPa.

During the measurement period the temperature shall be held stable to within ± 1 K.

The measured signals of the AMS shall be determined at each pressure by waiting the time equivalent to one independent reading and then recording three consecutive individual readings. The three individual readings shall be averaged.

The deviations between the average reading at each pressure and the average reading at the ambient atmospheric pressure shall be determined. The deviations shall meet the applicable performance criteria specified in [Table 1](#).

The individual readings, averages and deviations at each pressure as well as the maximum deviation shall be reported.

E.12 Influence of the sample gas flow for extractive AMS

The AMS shall initially be operated with the flow rate prescribed by the manufacturer. This flow rate shall then be changed to the lowest flow rate specified by the manufacturer.

NOTE Influence of the sample gas flow typically applies to extractive AMS, since in situ AMS mostly are not influenced by flow rate.

If the manufacturer's documentation permits only minor tolerances these are binding and shall not be extended.

The measured signals of the AMS at the zero point and span point shall be determined at both flow rates by waiting the time equivalent to one independent reading and then recording three consecutive individual readings. The three individual readings shall be averaged.

The deviation between the average readings at both flow rates shall be determined. The deviation shall meet the applicable performance criteria specified in [Table 1](#).

This test shall be repeated three times at the zero point and three times at the span point. If the AMS meets the performance criterion by a factor of two or more for the first test, then any subsequent testing may be omitted.

The individual readings, averages and the deviations as well as the maximum deviation shall be reported.

The functionality of the status signal shall be tested at the same time.

E.13 Sensitivity to ambient temperature, for a change of 10 K in the temperature range specified by the manufacturer

Determine how the zero and span values of the AMS are influenced by changes in ambient temperature by using a climatic chamber which can control ambient temperature from $-20\text{ }^{\circ}\text{C}$ to $+50\text{ }^{\circ}\text{C}$, within limits of $\pm 1,0\text{ K}$.

In the case of AMS installed outdoors, the following temperatures shall be set in the climatic chamber in the given order of sequence:

$20\text{ }^{\circ}\text{C} \rightarrow 0\text{ }^{\circ}\text{C} \rightarrow -20\text{ }^{\circ}\text{C} \rightarrow 20\text{ }^{\circ}\text{C} \rightarrow 50\text{ }^{\circ}\text{C} \rightarrow 20\text{ }^{\circ}\text{C}$.

In the case of AMS installed at temperature-controlled locations, the following temperatures shall be set in the given order of sequence:

$20\text{ }^{\circ}\text{C} \rightarrow 5\text{ }^{\circ}\text{C} \rightarrow 20\text{ }^{\circ}\text{C} \rightarrow 40\text{ }^{\circ}\text{C} \rightarrow 20\text{ }^{\circ}\text{C}$.

After a sufficient equilibration period, the measured signals of the AMS at zero point and at span point shall be determined at each temperature by waiting the time equivalent to one independent reading and then recording three consecutive individual readings. The three individual readings shall be averaged.

Wait at least 6 h between each temperature change in the environmental chamber, to allow the AMS to equilibrate, before taking further readings.

Alternatively, it is recommended to monitor the reading from the AMS following each temperature change. If the instrument stabilizes in less than six hours, then the test laboratory may reduce the equilibration period. However, record objective and verifiable evidence to support this.

The AMS shall remain switched on when varying the ambient temperature in the environmental chamber.

The deviations between the average reading at each temperature and the average reading at 20 °C shall be determined. The deviations shall meet the applicable performance criteria specified in 0 for all temperatures. The test shall be repeated three times at the zero point and three times at the span point. If the AMS meets the performance criterion by a factor of two or more for the first test, then any subsequent testing may be omitted.

The individual readings, averages and deviations at each temperature as well as the maximum deviation at zero point and at span point shall be reported.

E.14 Sensitivity to electric voltage

The supply voltage to the AMS shall be varied, using an isolating transformer, in steps of 5 % from the nominal supply voltage to at least the upper and the lower limits specified by the manufacturer. The measured signals of the AMS at zero point and at span point shall be determined at each voltage by waiting the time equivalent to one independent reading and then recording three consecutive individual readings. The three individual readings shall be averaged.

NOTE After changes in voltage the AMS can need time to stabilize. The deviations between the average reading at each voltage and the average reading at the nominal supply voltage shall be determined.

The deviations shall meet the applicable performance criteria specified in [Table 1](#) for all voltages. This test shall be repeated three times at the zero point and three times at the span point. If the AMS meets the performance criterion by a factor of two or more for the first test, then any subsequent testing may be omitted.

The individual readings, averages and deviations at each voltage as well as the maximum deviation at zero point and at span point shall be reported.

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Annex F (informative)

Examples of the results for the assessment of CO, CO₂ and O₂ AMS

F.1 CO measurement

The results of performance tests according to performance characteristics of [Annex E](#) for the CO measurement using cold extractive NDIR method ([Annex A](#)) and in situ TLS method ([Annex C](#)) are given in [Table F.1.1](#).

Note Most of the data listed in Tables from [F.1.1](#) to [F.3.2](#) have been taken from EN 15267 test reports (see Reference [\[9\]](#)).

Table F.1.1 — Examples of performance test results for CO measurement by using extractive NDIR methods and in situ TLS method

| Performance characteristic | Performance criterion | Cold extractive | | In situ |
|-----------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------|------------------------------------------|-----------------------------------|-----------------------|
| | | NDIR Cross-modulation type ^{a)} | NDIR dual-beam type ^{a)} | TLS type |
| Typical lowest range | | 50 mg/m ³ | 75 mg/m ³ | 250 mg/m ³ |
| Response time | ≤200 s | 57 s | 66 s | 1,6 s |
| Standard deviation of repeatability at zero point | ≤2 % of the upper limit of the lowest measuring range used | 0,6 % | 0,02 % | 0,1 % |
| Standard deviation of repeatability at span point | ≤2 % of the upper limit of the lowest measuring range used | 1,3 % | 0,05 % | 0,45 % |
| Lack-of-fit | ≤2 % of the upper limit of the lowest measuring range used | 0,60 % | -0,17 % | 0,96 % |
| Zero drift within 24 h | ≤2 % of the upper limit of the lowest measuring range used | — | — | 1,3 % |
| Span drift within 24 h | ≤2 % of the upper limit of the lowest measuring range used | — | — | 2,2 % |
| Zero drift within the period of unattended operation | ≤3 % of the upper limit of the lowest measuring range used | -0,4 % | 1,2 % | — |
| Span drift within the period of unattended operation | ≤3 % of the upper limit of the lowest measuring range used | 2,3 % | -2,0 % | — |
| Sensitivity to sample gas pressure, for a pressure change of 2 kPa | ≤3 % of the upper limit of the lowest measuring range used | — | — | — |
| Sensitivity to sample gas flow for extractive AMS | ≤2 % of the upper limit of the lowest measuring range used | -0,1 % | — | — |
| Sensitivity to ambient temperature, for a change of 10 K in the temperature range specified by the manufacturer | ≤3 % of the upper limit of the lowest measuring range used | 1,2 % | 2,7 % | 1,4 % |
| Sensitivity to electric voltage in the voltage range specified by the manufacturer | ≤2 % of the upper limit of the lowest measuring range used per 10V | 0,5 % | 0,10 % | 0,8 % |

^{a)} The data have been taken from EN 15267 test reports.

Table F.1.1 (continued)

| Performance characteristic | Performance criterion | Cold extractive | | In situ |
|--------------------------------------------------------------|---------------------------------------------------------------|------------------------------------------|-----------------------------------|----------|
| | | NDIR Cross-modulation type ^{a)} | NDIR dual-beam type ^{a)} | TLS type |
| Cross-sensitivity | ≤4 % of the upper limit of the lowest measuring range used | 2,6 % | -2,4 % | 1,5 % |
| Excursion of the measurement beam of cross-stack in situ AMS | ≤2 % of the measured value of the lowest measuring range used | — | — | — |

^{a)} The data have been taken from EN 15267 test reports.

F.2 CO₂ measurement

The results of performance tests according to performance characteristics of [Annex E](#) for the CO₂ measurement using extractive NDIR method ([Annex A](#)) and in situ TLS method ([Annex C](#)) are given in [Table F.2.1](#).

Table F.2.1 — Performance characteristics for CO₂ measurement by using extractive NDIR methods and in situ TLS method

| Performance characteristic | Performance criterion | Cold extractive | | In situ |
|--------------------------------------------------------------------|------------------------------------------------------------|------------------------------------------|-----------------------------------|---------------------------|
| | | NDIR Cross-modulation type ^{a)} | NDIR dual-beam type ^{a)} | TLS type |
| Typical lowest range | | 20 % (volume fraction) | 20 % (volume fraction) | 20 % (volume fraction) |
| Response time | ≤200 s | 58 s | 80 s | 1,6 s |
| Standard deviation of repeatability in laboratory at zero point | ≤2 % of the upper limit of the lowest measuring range used | 0,0 % | 0,0 % | 0,07 % |
| Standard deviation of repeatability in laboratory at span point | ≤2 % of the upper limit of the lowest measuring range used | 0,1 % | 0,05 % | 0,07 % |
| Lack-of-fit | ≤2 % of the upper limit of the lowest measuring range used | 1,00 % | 0,35 % | 1,9 % |
| Zero drift within 24 h | ≤2 % of the upper limit of the lowest measuring range used | — | — | -0,2 % |
| Span drift within 24 h | ≤2 % of the upper limit of the lowest measuring range used | — | — | 1,6 % |
| Zero drift within the period of unattended operation | ≤3 % of the upper limit of the lowest measuring range used | -0,6 % | 0,10 % | — |
| Span drift within the period of unattended operation | ≤3 % of the upper limit of the lowest measuring range used | 2,7 % | -1,8 % | — |
| Sensitivity to sample gas pressure, for a pressure change of 2 kPa | ≤3 % | — | — | — |
| Sensitivity to sample gas flow for extractive AMS | ≤2 % | 0,1 % | — | — |

^{a)} The data has been taken from EN 15267 test reports.