
**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 O₂ 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.

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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