



**International
Standard**

ISO 7935

**Stationary source emissions —
Determination of the mass
concentration of sulfur dioxide
in flue gases — Performance
characteristics of automated
measuring systems**

*Émissions de sources fixes — Détermination de la concentration
en masse de dioxyde de soufre — Caractéristiques de
performance des systèmes de mesurage automatiques*

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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 document 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).

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For an explanation of 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 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 7935:1992), which has been technically revised.

The main changes are as follows:

- the structure and the components have been updated to be similar to the latest editions of e.g. ISO 10849 (measurement of nitrogen oxides), ISO 12039 (measurement of CO, CO₂ and O₂), ISO 17179 (measurement of NH₃), ISO 13199 (measurement of total VOC), ISO 25140 (measurement of CH₄), ISO 21258 (measurement of N₂O);
- [Clause 3](#) has been revised with the addition or deletion and change in terms and definitions;
- a new analytical technique has been added (laser spectroscopic technique or tunable laser spectroscopy) for measurement of SO₂;
- the performance characteristics and criteria as well as QA/QC procedures have been changed to harmonize with latest ISO standards;
- examples of performance test results and the results of uncertainty calculation have been added for SO₂ 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

Sulfur dioxide (SO₂) can arise in considerable quantities from combustion of fossil fuels used for energy generation, industrial activities processing sulfur or sulfur containing material, and from combustion of sulfur containing waste. The waste gas from these processes, containing sulfur dioxide, is usually discharged into the ambient atmosphere, via a duct or a chimney.

For evaluating the mass concentration of sulfur dioxide present in the waste gas of stationary source emissions, a number of highly developed methods of integrated sampling and subsequent determination by chemical analysis and automated measuring systems are available.

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Stationary source emissions — Determination of the mass concentration of sulfur dioxide in flue gases — Performance characteristics of automated measuring systems

1 Scope

This document specifies a method for the determination of sulfur dioxide (SO₂) in flue gases of stationary sources and describes the fundamental structure and the key performance characteristics of automated measuring systems.

The method allows continuous monitoring with permanently installed measuring systems of SO₂ emissions.

This document describes extractive systems and in situ (non-extractive) systems in connection with a range of analysers that operate using, for example, the following principles:

- non-dispersive infrared absorption (NDIR);
- Fourier transform infrared (FTIR) spectroscopy;
- laser spectroscopic technique or tunable laser spectroscopy (TLS);
- non-dispersive ultraviolet absorption (NDUV);
- differential optical absorption spectroscopy (DOAS).

Other equivalent instrumental methods can be used provided they meet the minimum performance requirements specified in this document. The measuring system can be validated with reference materials, according to this document, or comparable methods.

Automated measuring system (AMS) based on the principles listed above has been used successfully in this application for the measuring ranges as shown in [Annex E](#).

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

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

3 Terms and definitions

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

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <https://www.electropedia.org/>

3.1

analyser

analytical part in an extractive or *in situ automated measuring system* (3.3)

[SOURCE: ISO 12039:2019,^[2] 3.1]

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* (3.9) in unattended operation

Note 1 to entry: For the purposes 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 SO₂ passing through the duct.

[SOURCE: ISO 9169:2006, 2.1.2, modified — Note 1 to entry has been replaced.]

3.3

in situ AMS

non-extractive system that measures 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 under test and with the reference method at points a short distance from each other, providing pairs of measured values

Note 1 to entry: See 3.20.

3.5

independent reading

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

3.6

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

3.7

interferent

interfering substance

substance present in the air mass under investigation, other than the *measurand* (3.9), that affects the response of AMS (3.2)

3.8

lack-of-fit

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

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

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, modified — Note 2 to entry has been removed.]

3.9

measurand

particular quantity subject to measurement

[SOURCE: ISO/IEC Guide 98-3:2008^[6], B.2.9, modified — Example and Note 1 to entry have been removed.]

3.10

performance characteristic

quantity assigned to equipment in order to define its performance

Note 1 to entry: Performance characteristics can be described by values, tolerances or ranges.

3.11

period of unattended operation

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

[SOURCE: ISO 9169:2006, 2.2.11]

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

3.12

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] 3.20]

3.13

reference method

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

Note 1 to entry: See [3.4](#).

3.14

transport time in the measuring line

time period for transportation of the sampled gas from the inlet of the probe to the inlet of the measurement instrument

3.15

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.

3.16

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: The concentration is often chosen around 70 % to 90 % of full scale.

3.17

span point

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

3.18

standard uncertainty

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

[SOURCE: ISO/IEC Guide 98-3:2008^[6], 2.3.1]

3.19

uncertainty

parameter associated with the result of a measurement, that characterizes the dispersion of the values that can reasonably be attributed to the measurand

[SOURCE: ISO/IEC Guide 98-3:2008^[6], 2.2.3 modified — Notes 1, 2 and 3 to entry have been removed.]

3.20

validation of an automated measuring system

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

3.21

zero gas

gas or gas mixture used to establish the *zero point* (3.22) on a calibration curve within a given concentration range

[SOURCE: ISO 12039:2019,^[2] 3.20]

3.22

zero point

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

4 Symbols and abbreviated terms

4.1 Symbols

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 (SO ₂) mass concentration
$U(\gamma_X)$	Expanded uncertainty of X (SO ₂) mass concentration
M_x	Molar mass of X (SO ₂ , g/mol)
V_M	Molar volume (22,4 l/mol at standard conditions, 273,15 K; 101,325 kPa)
φ_X	Volume fraction of X (SO ₂)
γ_X	SO ₂ mass concentration at standard conditions in mg/m ³ (273,15 K; 101,325 kPa)
γ_R	SO 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
\hat{x}_i	Value estimated by the regression line at level i

4.2 Abbreviated terms

AMS	Automated measuring system
FTIR	Fourier transform infrared
TLS	Tunable laser spectroscopy
NDIR	Non-dispersive infrared
NDUV	Non-dispersive ultraviolet
DOAS	Differential optical absorption spectroscopy
UVF	Ultraviolet fluorescence
QA	Quality assurance
QC	Quality control

5 Principle

This document describes automated measurement systems for sampling, sample conditioning and determining SO₂ content in flue gas using instrumental methods (analysers).

There are two types of automated measuring systems:

- extractive systems;
- in situ systems.

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

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

The systems described in this document measure SO₂ concentrations using instrumental methods that shall meet the minimum performance specifications given.

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^[1].

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 as well as non-extractive systems are described in ISO 10396^[1]:

- cold-dry,
- hot-wet, and
- dilution.

In non-extractive sampling, the measurements are made in situ; therefore, no sample conditioning is required.

The details of the extractive sampling and sample gas conditioning systems are described in [Annex A](#) and two kinds of in situ system are illustrated in [Annex B](#).

6.2 Analyser equipment

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

AMS shall meet the performance characteristics as 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 test, 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 SO₂

Performance characteristic	Performance criterion	Test procedure
Response time	≤200 s	D.2
Standard deviation of repeatability in laboratory at zero point	≤2,0 % of the upper limit of the lowest measuring range used	D.3.2
Standard deviation of repeatability in laboratory at span point	≤2,0 % of the upper limit of the lowest measuring range used	D.3.3
Lack-of-fit	≤2,0 % of the upper limit of the lowest measuring range used	D.4
Zero drift within 24 h	≤2,0 % of the upper limit of the lowest measuring range used	D.5
Span drift within 24 h	≤2,0 % of the upper limit of the lowest measuring range used	D.5
Zero drift within the period of unattended operation	≤3,0 % of the upper limit of the lowest measuring range used	D.6
Span drift within the period of unattended operation	≤3,0 % of the upper limit of the lowest measuring range used	D.6
Sensitivity to ambient temperature, for a change of 20 K in the temperature range specified by the manufacturer	≤5,0 % of the upper limit of the lowest measuring range used	D.7
Sensitivity to sample gas pressure, for a pressure change of 3 kPa	≤2,0 % of the upper limit of the lowest measuring range used	D.8
Sensitivity to sample gas flow for an extractive AMS	≤2,0 % of the upper limit of the lowest measuring range used	D.9
Sensitivity to electric voltage in the range -15 % below or +10 % above from the nominal voltage stated by the manufacturer	≤2,0 % of the upper limit of the lowest measuring range used	D.10
Cross-sensitivity	≤4,0 % of the upper limit of the lowest measuring range used	D.11
Losses and leakage in the sampling line and conditioning system	≤2,0 % of the measured value	D.12 and D.13
Excursion of the measurement beam of cross-stack in situ AMS	≤2 % of the measured value of the lowest measuring range used	D.14

7.2 Determination of the performance characteristics

7.2.1 Performance test

The performance characteristics of the AMS shall be determined during the performance test. The values of the performance characteristics determined shall meet the performance criteria specified in [Table 1](#). The procedures for the determination of these performance characteristics are specified in [Annex D](#).

The ambient conditions applied during the general performance test 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, 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.^[5] 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 reference materials 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 flue gas;
- expected concentration range of SO₂;
- 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^[3] and ISO 14385-2^[4].

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 the safety of the personnel involved.

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, for example, in ISO 10396,^[1] where gas stratification, fluctuations in gas velocity, temperature and others are discussed.

8.3 Calculation of conversion from volume to mass concentration for SO₂

Results of the measurement for SO₂ shall be expressed as mass concentrations at reference conditions.

If the SO₂ concentration is provided as a volume fraction, [Formula \(1\)](#) shall be used to convert volume fraction of SO₂ (10⁻⁶), $\varnothing_{\text{SO}_2}$, to SO₂ mass concentrations, γ_{SO_2} :

$$\gamma_{\text{SO}_2} = \varnothing_{\text{SO}_2} \cdot \frac{M_{\text{SO}_2}}{V_M} \quad (1)$$

where

γ_{SO_2} is the SO₂ mass concentration in mg/m³ at standard conditions (273,15 K; 101,325 kPa);

$\varnothing_{\text{SO}_2}$ is the volume fraction of SO₂ (by volume, 10⁻⁶);

M_{SO_2} is the molar mass of SO₂ (= 64,06 g/mol);

V_M is the molar volume (= 22,4 l/mol at 273,15K and 101,325 kPa).

If necessary, the SO₂ concentration measured in the wet gas should be corrected to the SO₂ concentration at standard conditions (dry gas), using [Formula \(2\)](#):

$$\gamma_R = \gamma_{\text{SO}_2} \cdot \frac{100 \%}{100 \% - h} \quad (2)$$

where

γ_R is the SO₂ mass concentration at standard conditions in mg/m³ (273,15 K; 101,325 kPa; H₂O corrected);

h is the absolute water vapour content (by volume) (%).

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 SO₂ is kept within the limits specified for the measurement task. The results of the QA/QC procedures shall be documented.