



SLOVENSKI STANDARD
oSIST prEN 14791:2015
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**Emisije nepremičnih virov - Določevanje masne koncentracije žveplovih dioksidov
- Standardna referenčna metoda**

Stationary source emissions - Determination of mass concentration of sulphur oxides -
Standard reference method

Emissionen aus stationären Quellen - Bestimmung der Massenkonzentration von
Schwefeloxiden - Standardreferenzverfahren

Emissions de sources fixes - Détermination de la concentration massique des oxydes de
soufre - Méthode de référence normalisée

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Stationary source emissions - Determination of mass concentration of sulphur oxides - Standard reference method

Emissions de sources fixes - Détermination de la concentration massique des oxydes de soufre - Méthode de référence normalisée

Emissionen aus stationären Quellen - Bestimmung der Massenkonzentration von Schwefeloxiden - Standardreferenzverfahren

This draft European Standard is submitted to CEN members for enquiry. It has been drawn up by the Technical Committee CEN/TC 264.

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Foreword

This document (prEN 14791:2014) has been prepared by Technical Committee CEN/TC 264 “Air quality”, the secretariat of which is held by DIN.

This document is currently submitted to the CEN Enquiry.

This document will supersede EN 14791:2005.

Annex G provides details of significant technical changes between this document and the previous edition.

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prEN 14791:2014 (E)**1 Scope**

This European Standard specifies the standard reference method (SRM) for the determination of the sulphuric oxide SO₂ in flue gases emitted to the atmosphere from ducts and stacks. It is based on a sampling system and two analytical principles: ion chromatography and the Thorin method.

This European Standard specifies the performance characteristics to be determined and the performance criteria to be fulfilled by measuring systems based on the measurement method. It applies to periodic monitoring and to the calibration or control of automatic measuring systems (AMS) permanently installed on a stack, for regulatory or other purposes.

This European Standard specifies criteria for demonstration of equivalence of an alternative method to the SRM by application of prEN 14793.

This European Standard has been evaluated during field tests on waste incineration, co-incineration and large combustion installations. It has been validated for sampling periods of 30 min in the range of 0,5 mg/m³ to 2 000 mg/m³ of SO₂ for an ion-chromatography variant and 5 mg/m³ to 2 000 mg/m³ of SO₂ for the Thorin method according to emission limit values laid down in the Directive 2010/75/EC.

The limit values of EU Directives are expressed in units of mg/m³ of SO₂ on dry basis and at standard conditions of 273 K and 101,3 kPa.

NOTE The characteristics of installations, the conditions during field tests and the values of repeatability and reproducibility in the field are given in Annex E.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

prEN 14793:2014, *Stationary source emission – Demonstration of equivalence of an alternative method with a reference method*

EN 15259:2007, *Air quality – Measurement of stationary source emissions – Requirements for measurement sections and sites and for the measurement objective, plan and report*

EN ISO 14956:2002, *Air quality – Evaluation of the suitability of a measurement procedure by comparison with a required measurement uncertainty (ISO 14956:2002)*

ISO/IEC Guide 98-3:2008, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

3 Terms and definitions

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

3.1**absorber**

device in which sulphur oxide is absorbed into an absorption liquid

3.2 absorption efficiency

ε

ratio of quantity of the analyte q_1 collected in the first absorber divided by the quantity of the analyte collected in the first and the second absorber ($q_1 + q_2$)

$$\varepsilon = q_1 / (q_1 + q_2)$$

3.3 automated measuring system AMS

measuring system permanently installed on site for continuous monitoring of emissions or measurement of peripheral parameters

Note 1 to entry: An AMS is a method which is traceable to a reference method.

Note 2 to entry: Apart from the analyser, an AMS includes facilities for taking samples (e.g. probe, sample gas lines, flow meters, regulators, delivery pumps) and for sample conditioning (e.g. dust filter, moisture removal devices, converters, diluters). This definition also includes testing and adjusting devices that are required for regular functional checks.

[SOURCE: FprEN 14181:2014]

3.4 calibration of an AMS

establishment of the statistical relationship between values of the measurand indicated by the automated measuring system (AMS) and the corresponding values given by the standard reference method (SRM) used during the same period of time and giving a representative measurement on the same measurement plane

Note 1 to entry: The result of calibration permits to establish the relationship between the values of the SRM and the AMS (calibration function).

Note 2 to entry: Calibration should not be confused with adjustment of a measuring system.

3.5 calibration of the SRM

set of operations that establish, under specified conditions, the relationship between values of quantities indicated by a measuring instrument or measuring system, and the corresponding values realized by standard reference method implemented in the state of the art in order to provide representative results.

3.6 chemical blank value

sulphate ion content of an unexposed sample of the absorption solution, plus reagents that are added to the solution before analysis if necessary

3.7 emission limit value ELV

emission limit value according to EU Directives on the basis of 30 min, 1 h or 1 day

3.8 field blank

value determined by a specific procedure used to ensure that no significant contamination has occurred during all steps of the measurement and to check that the operator can achieve a quantification level adapted to the task

[SOURCE: CEN/TS 15675]

prEN 14791:2014 (E)**3.9****influence quantity**

quantity that is not the measurand but that affects the result of the measurement

Note 1 to entry: Influence quantities are e.g. ambient temperature, atmospheric pressure, presence of interfering gases in the flue gas matrix or pressure of the gas sample.

3.10**measurand**

quantity intended to be measured

[SOURCE: JCGM 200:2012]

3.11**measurement series**

several successive measurements carried out on the same measurement plane and at the same process operating conditions

3.12**measurement plane**

plane normal to the centreline of the duct at the sampling position

Note 1 to entry: Measurement plane is also known as sampling plane.

[SOURCE: EN 15259:2007]

3.13**measurement point**

position in the measurement plane at which the sample stream is extracted or the measurement data are obtained directly

Note 1 to entry: Measurement point is also known as sampling point.

[SOURCE: EN 15259:2007]

3.14**measurement site**

place on the waste gas duct in the area of the measurement plane(s) consisting of structures and technical equipment, for example working platforms, measurement ports, energy supply

Note 1 to entry: Measurement site is also known as sampling site.

[SOURCE: EN 15259:2007]

3.15**measuring system**

complete set of measuring instruments and other equipment assembled to carry out specified measurements

[VIM 3.2]

3.16**performance characteristic**

one of the quantities (described by values, tolerances, range, ...) assigned to equipment in order to define its performance

3.17**reference method****RM**

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

Note 1 to entry: A reference method is fully described.

Note 2 to entry: A reference method can be a manual or an automated method.

Note 3 to entry: Alternative methods can be used if equivalence to the reference method has been demonstrated.

[SOURCE: EN 15259:2007]

3.18**standard reference method****SRM**

reference method prescribed by European or national legislation

[SOURCE: EN 15259:2007]

3.19**repeatability in the laboratory**

closeness of the agreement between the results of successive measurements of the same measurand carried out under the same conditions of measurement

Note 1 to entry: These conditions include:

- same measurement procedure;
- same laboratory;
- same sampling equipment, used under the same conditions;
- same location;
- repetition over a short period of time.

Note 2 to entry: Repeatability may be expressed quantitatively in terms of the dispersion characteristics of the results.

Note 3 to entry: In this European Standard the repeatability is expressed as a value with a level of confidence of 95 %.

3.20**repeatability in the field**

closeness of the agreement between the results of simultaneous measurements of the same measurand carried out with two equipments under the same conditions of measurement

Note 1 to entry: These conditions include:

- same measurement procedure;
- two equipments, the performances of which are fulfilling the requirements of the reference method, used under the same conditions;
- same location;
- implemented by the same laboratory;
- typically calculated on short periods of time in order to avoid the effect of changes of influence parameters (e.g. 30 min).

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Note 2 to entry: Repeatability may be expressed quantitatively in terms of the dispersion characteristics of the results.

Note 3 to entry: In this European Standard the repeatability under field conditions is expressed as a value with a level of confidence of 95 %.

3.21**reproducibility in the field**

closeness of the agreement between the results of simultaneous measurements of the same measurand carried out with several sets of equipment under the same conditions of measurement

Note 1 to entry: These conditions are called field reproducibility conditions and include:

- same measurement procedure;
- several sets of equipment, the performance of which fulfils the requirements of the reference method, used under the same conditions;
- same location;
- implemented by several laboratories.

Note 2 to entry: Reproducibility may be expressed quantitatively in terms of the dispersion characteristics of the results.

Note 3 to entry: In this European Standard the reproducibility under field conditions is expressed as a value with a level of confidence of 95 %.

3.22**uncertainty**

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

3.23**standard uncertainty**

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

3.24**combined uncertainty**

u_c
standard uncertainty attached to the measurement result calculated by combination of several standard uncertainties according to the principles laid down in ISO/IEC Guide 98-3 (GUM)

3.25**expanded uncertainty**

U
quantity defining a level of confidence about the result of a measurement that may be expected to encompass a specific fraction of the distribution of values that could reasonably be attributed to a measurand

$$U = k \times u$$

Note 1 to entry: In this European Standard, the expanded uncertainty is calculated with a coverage factor of $k = 2$, and with a level of confidence of 95 %.

Note 2 to entry: The expression overall uncertainty is sometimes used to express the expanded uncertainty.

3.26**uncertainty budget**

calculation table combining all the sources of uncertainty according to EN ISO 14956 or ISO/IEC Guide 98-3 in order to calculate the combined uncertainty of the method at a specified value

4 Symbols and abbreviated terms

4.1 Symbols

For the purposes of this document, the following symbols apply.

C_m	mass concentration of sulphur dioxide in the sample gas, in milligrams per cubic metre (of gas)
f_a	equivalent mass of sulphur dioxide of 1 mm of titration solution (barium perchlorate standard volumetric solution) used for titration in Thorin method, in milligrams per millilitre
f_v	ratio of the volume of the pre-treated sample solution (sample absorption solution pre-treated before analyse) to the volume of the aliquot taken for the titration in Thorin method
L_Q	limit of quantification, in milligrams per litre of SO_4^{2-}
m_s	weight of the sample solution (absorption solution used for sampling + rinsing solution), in grams
P_m	absolute pressure at the gas volume meter, in kilopascals
P_{std}	standard pressure: 101,3 kPa
$P_{\text{sat}}(T_m)$	saturation vapour pressure of water at volume gas meter temperature, in kilopascals
q_s	mass concentration of sulphate in sample absorption solution, in milligrams per litre (of solution)
q_{cb}	mass concentration of sulphate in chemical blank solution, in milligrams per litre (of solution)
r	repeatability, in milligrams per cubic metre or percentage
R	reproducibility, in milligrams per cubic metre or percentage
R_s	peak resolution S_s : volume of titration solution used for titration of sample absorption solution, in millilitre
S_{cb}	volume of titration solution used for titration of chemical blank solution, in millilitre
S_r	repeatability standard deviation, in milligrams per cubic metre or percentage
S_R	reproducibility standard deviation, in milligrams per cubic metre or percentage
$S_{r, \text{limit}}$	maximum allowable repeatability standard deviation, in milligrams per cubic metre
S_s	volume of titration solution used for the titration of the aliquot of the pre-treated sample solution, in millilitres
t_1	retention time of the first peak, in seconds
t_2	retention time of the second peak, in seconds
T_j	temperature at the gas meter, in Kelvin
T_m	mean temperature at the gas volume meter, in Kelvin

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T_{std}	standard temperature, 273 K
V_1	reading at the gas volume meter at the beginning of the sampling period, in cubic metres
V_2	reading at the gas volume meter at the end of the sampling period, in cubic metres
$V_{\text{m (std)}}$	dry gas volume measured, corrected to standard conditions, in cubic metres
V_{s}	volume of the sample solution (absorption solution used for sampling + rinsing solution), in litres
w_1	peak width, on the time axis, of the first peak, in seconds
w_2	peak width on the time axis, of the second peak, in seconds
ε	absorption efficiency, in percentage
σ	conductivity, in micro-siemens per metre
ρ_{20}^4	density of a liquid at 20 °C compared to water's at 4 °C, in kilograms per litre
χ	volume content, in percentage

4.2 Abbreviated terms

For the purposes of this document, the following abbreviated terms apply.

PE	Polyethene
PTFE	Polytetrafluoroethene

5 Measuring principle**5.1 General**

This European Standard describes the standard reference method (SRM) based on two alternative analytical techniques for determining sulphur dioxide (SO₂) content emitted to atmosphere from ducts and stacks. The specific components and the requirements for the measuring system are described in Clauses 6 to Clause 8. A number of performance characteristics with associated performance criteria are specified for the measuring system (see Tables 1 and 2). The expanded uncertainty of the method shall meet the specifications given in this European Standard. Requirements and recommendations for quality assurance and quality control are given for measurements in the field (see Clause 6 and Clause 8).

5.2 Measuring principle

A sample of gas is extracted via a heated temperature-controlled probe. The sample is filtered and drawn through hydrogen peroxide absorber solutions for a specified time and at a controlled flow rate. The sulphur dioxide in the sampled gas is absorbed and oxidised to sulphate ion. The mass concentration of sulphate in the absorption solutions is subsequently determined using ion chromatography or by titration with a barium perchlorate solution using Thorin as indicator. SO₃ is also absorbed and transformed in sulphate ion and is therefore an interferent.

This European Standard has been validated with a 0,3 % H₂O₂ absorption solution for concentrations lower than 1 000 mg/m³ and with a 3,0 % H₂O₂ absorption solution for higher concentrations but lower than 2 000 mg/m³. Typical concentration of the absorption solution is 0,3 % H₂O₂. However, for concentrations higher than 1 000 mg/m³ it is recommended, in case of a bad efficiency either to decrease the flow or to increase the H₂O₂ concentration.

6 Description of measuring equipment

6.1 Reagents

6.1.1 General

During the analysis, use only reagents of recognised analytical grade.

Normal, accepted laboratory safety practices and cleaning procedures for glassware should be followed during reagent preparation.

WARNING — Use the reagents in accordance with the appropriate health and safety regulations.

6.1.2 Hydrogen peroxide

Commercially available solution of H₂O₂; mass content 30 %, $\rho_{20}^4 = 1,11$ kg/l.

6.1.3 Water

H₂O; ultra pure water with conductivity $\sigma < 10$ $\mu\text{S m}^{-1}$.

6.1.4 Absorption solution, H₂O₂

The absorption solution is a hydrogen peroxide solution (6.1.2) diluted to a mass concentration of 0,3 % H₂O₂ in water (6.1.3). For flue-gas concentrations higher than 1 000 mg/m³, it is suggested, in case of a bad efficiency, either to decrease the flow, or to increase the concentration of the absorption solution.

For the preparation of the mass concentration of 0,3 % H₂O₂ in water, thoroughly mix about 10 ml of 30 % of H₂O₂ (6.1.2) with 500 ml of water (6.1.3) and make up to 1 000 ml with water (6.1.3). Store the solution in a glass or PE bottle in a dark place and for no longer than one week.

WARNING — Decomposition of the solution may occur and may lead to the explosion of the storage bottle. It is recommended that the lid of this bottle is not closed too tightly or to use a security cap.

NOTE Cleanliness of the glassware is important to avoid a possible decomposition of hydrogen peroxide.

6.1.5 Reagents for chromatographic analysis

6.1.5.1 Eluent solution

The choice of eluent depends on the manufacturer's separator column and detector. For the exact composition of the eluent, use a validated solvent for the method and/or refer to the instructions given by the manufacturer.

NOTE For an ion chromatograph using the suppressor technique, a typical eluent is a solution of $1,7 \times 10^{-3}$ mol/l of NaHCO₃ and $1,8 \times 10^{-3}$ mol/l of Na₂CO₃.

prEN 14791:2014 (E)**6.1.5.2 Standard sulphate stock solution, $10,4 \times 10^{-3}$ mol/l of SO_4^{2-}**

Use a commercially available sulphate stock solution of 1 000 mg/l sulphate ($10,4 \times 10^{-3}$ mol/l) with a minimum content of 99,0 %. As an alternative prepare the standard solution as follows:

Dissolve 1,814 g of analytical grade potassium sulphate (K_2SO_4) in water (6.1.3) and dilute to a 1 000 ml volumetric flask. 1 ml of stock solution corresponds to 1 mg of SO_4^{2-} .

NOTE Calibration standards are prepared by diluting the standard stock solution with the absorption solution as specified in 9.2.3.2.

6.1.5.3 Regeneration solution for suppressor

For the exact composition of the suppressor regeneration solution, refer to the instructions given by the manufacturer of the suppressor.

NOTE An example is a solution of $12,5 \times 10^{-3}$ mol/l of H_2SO_4 .

6.1.6 Reagent for Thorin analysis**6.1.6.1 2-propanol [$\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$]**

Use commercially available 2-propanol [$\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$] in analytical grade (minimum content 99,8 %).

6.1.6.2 Barium perchlorate, standard volumetric solution, $[\text{Ba}(\text{ClO}_4)_2] = 0,005$ mol/l

Use a commercially available barium perchlorate solution (80 % 2-propanol/20 % water) with concentration of 0,005 mol/l $\text{Ba}(\text{ClO}_4)_2$, or prepare the standard solution as follows:

Dissolve 1,7 g of anhydrous barium perchlorate [$\text{Ba}(\text{ClO}_4)_2$] in about 200 ml of water in a 1 000 ml one-mark volumetric flask. Make up to the mark with 2-propanol (5.1.6.1) and mix well.

Titrate the solution accurately against a 0,005 mol/l standard volumetric sulphuric acid solution.

1 ml of exactly 0,005 mol/l barium perchlorate solution is equivalent to a mass of sulphur dioxide of 0,320 mg; ($f_a = 0,320$ mg/ml).

6.1.6.3 Potassium hydroxide, standard volumetric solution, $[\text{KOH}] = 0,1$ mol/l

Use a commercially available solution of 0,1 mol/l KOH in water.

NOTE This reagent is only necessary if the sampling gas contains high concentration of acid components (e.g. $\text{SO}_2 > 100$ mg/m³ or HCl > 200 mg/m³ or $\text{NO}_2 > 400$ mg/m³).

6.1.6.4 Perchloric acid, standard volumetric solution, $[\text{HClO}_4] = 0,1$ mol/l

Prepare an approximate 1 % solution of perchloric acid by mixing 16 ml of a commercially available solution of 60 % perchloric acid in water (6.1.3) and make up to 1 000 ml with water. Store this solution in a glass or PE bottle.

NOTE This reagent is only necessary if the sampling gas contents high concentrations of alkali components (e.g. $\text{NH}_3 > 50$ mg/m³).

6.1.6.5 Thorin, {4-[2-arsonophenyl]-azo]-3-hydroxy-2,7 naphthalene-disulfonic acid disodium salt} 2 g/l solution

Thorin is also known as Thoron or Thoronol, the sodium salt of -1(2-arsonophenyl)-azol-3 -hydroxy-2,7-naphthalene-disulfonic acid.

Dissolve 0,2 g of Thorin in water (6.1.3) in a 100 ml one-mark volumetric flask. Make up to the mark with water and mix well.

Store this solution in a bottle made of glass or polyethylene.

6.2 Sampling equipment

6.2.1 General

A known volume of flue gas is extracted representatively from a duct or a chimney during a certain period of time at a controlled flow rate. A filter removes the dust in the sampled volume, thereafter the gas stream is passed through a series of absorbers containing an absorption solution.

All parts of the sampling equipment upstream of the first absorber shall not react with or adsorb SO_2 (i.e. borosilicate glass, quartz glass, PTFE or titanium are suitable materials).

If an unheated gas connector line is used between the heated filter and the first absorber, it shall be thoroughly rinsed with fresh absorption solution after sampling and the rinsing solutions shall be combined with the sample.

An example of a suitable sampling train is shown in Figure A.1.

6.2.2 Sampling probe

In order to reach the measurement point(s) of the measurement plane, probes of different lengths and inner diameters may be used. The design and configuration of the probe used shall ensure the residence time of the sample gas within the probe is minimised in order to reduce the response time of the measuring system.

NOTE 1 The probe may be marked before sampling in order to demonstrate that the measurement point(s) in the measurement plane has (have) been reached.

When droplets are present in the flue gases, they may contain SO_2 dissolved in it. In that case, the probe is equipped with a nozzle and an isokinetic sampling shall be performed according to EN 13284-1.

NOTE 2 It is possible to perform the sampling of SO_2 and HCl simultaneously with the same probe without nozzle providing no droplets are present.

NOTE 3 SO_2 and H_2O can be measured simultaneously by using the same probe without nozzle and the same side stream absorbers, providing no droplets are present in the flue gases.

The sampling probe shall be surrounded by a heating jacket capable of producing a controlled temperature of at least $120\text{ }^\circ\text{C}$ or $20\text{ }^\circ\text{C}$ higher than the (acid) dew point of gases and shall be protected and positioned using an outer tube.

6.2.3 Filter housing

The filter housing may be located either:

- directly in front of the probe behind the entry nozzle (in-stack filtration); or
- directly behind the probe (out-stack filtration).