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SLOVENSKI STANDARD
oSIST prEN 14212:2022

01-december-2022

Zunanji zrak - Standardna metoda za določanje koncentracije žveplovega dioksida z ultravijolično fluorescenco

Ambient air - Standard method for the measurement of the concentration of sulphur dioxide by ultraviolet fluorescence

Außenluft - Messverfahren zur Bestimmung der Konzentration von Schwefeldioxid mit Ultraviolett-Fluoreszenz

Air ambiant - Méthode normalisée pour le mesurage de la concentration en dioxyde de soufre par fluorescence U.V.

Ta slovenski standard je istoveten z: prEN 14212

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13.040.20   Kakovost okoljskega zraka   Ambient atmospheres

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English Version

Ambient air - Standard method for the measurement of the concentration of sulphur dioxide by ultraviolet fluorescence

Air ambiant - Méthode normalisée pour le mesurage de la concentration en dioxyde de soufre par fluorescence U.V.

Außenluft - Messverfahren zur Bestimmung der Konzentration von Schwefeldioxid mit Ultraviolett-Fluoreszenz

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

If this draft becomes a European Standard, CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration.

This draft European Standard was established by CEN in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the CEN-CENELEC Management Centre has the same status as the official versions.

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Recipients of this draft are invited to submit, with their comments, notification of any relevant patent rights of which they are aware and to provide supporting documentation.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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prEN 14212:2022 (E)

Contents

Page

2

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prEN 14212:2022 (E)

European foreword

This document (prEN 14212:2022) 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 14212:2012.

The technical modifications in comparison with the previous edition are listed in Annex J of this document.

1 Scope

This document specifies a continuous measurement method for the determination of the concentration of sulfur dioxide present in ambient air based on the ultraviolet fluorescence measuring principle. This document describes the performance characteristics and sets the relevant minimum criteria required to select an appropriate ultraviolet fluorescence analyser by means of type testing. It also includes the evaluation of the suitability of an analyser for use in a specific fixed site so as to meet the data quality requirements as specified in Annex I of Directive 2008/50/EC [1] and requirements during sampling, calibration and quality assurance for use.

The method is applicable to the determination of the mass concentration of sulphur dioxide present in ambient air up to 1000 µg/m^3. This concentration range represents the certification range for sulfur dioxide for type testing.

NOTE 1   It is possible to use other ranges depending on the levels present in ambient air.

NOTE 2   When this document is used for purposes other than for measurements required by Directive 2008/50/EC, the ranges and uncertainty requirements possibly do not apply.

The method covers the determination of ambient air concentrations of sulfur dioxide in locations classified as rural areas, urban-background areas, and for sampling influenced by traffic or industrial sources.

The results are expressed in µg/m^3 (at 20 °C and 101,3 kPa).

NOTE 3   1 000 µg/m^3 of SO_2 corresponds to 376 nmol/mol of SO_2.

This document contains information for different groups of users.

Clause 5 to Clause 7 and Annex C and Annex D contain general information about the principles of sulfur dioxide measurement by ultraviolet fluorescence analyser and sampling equipment.

Clause 8 and Annex E are specifically directed towards test houses and laboratories that perform type testing of sulfur dioxide analysers. These sections contain information about:

— type testing conditions, test procedures and test requirements;

— analyser performance requirements;

— evaluation of the type testing results;

— evaluation of the uncertainty of the measurement results of the sulfur dioxide analyser based on the type testing results.

Clause 9 to Clause 11 and Annex F and Annex G are directed towards monitoring networks performing the practical measurements of sulfur dioxide in ambient air. These sections contain information about:

— initial installation of the analyser in the monitoring network and acceptance testing;

— ongoing quality assurance/quality control;

— calculation and reporting of measurement results;

— evaluation of the uncertainty of the measurement results under practical monitoring conditions.

This document represents an evolution of earlier editions (EN 14212:2005 and EN 14212:2012). It is advisable that when equipment is procured it complies fully with this document.

NOTE 4   Type testing performed prior to the publication of this document for the purpose of demonstrating equivalence are still valid.

NOTE 5   Analysers type tested prior to the publication of this document remain valid for use for regulated monitoring purposes.

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.

EN 15267-1, *Air quality - Certification of automated measuring systems - Part 1: General principles*

EN 15267-2, *Air quality - Certification of automated measuring systems - Part 2: Initial assessment of the AMS manufacturer's quality management system and post certification surveillance for the manufacturing process*

EN ISO 6142, *Gas analysis — Preparation of calibration gas mixtures — Gravimetric method (ISO 6142)*

EN ISO 6143, *Gas analysis - Comparison methods for determining and checking the composition of calibration gas mixtures (ISO 6143)*

EN ISO 6144, *Gas analysis - Preparation of calibration gas mixtures - Static volumetric method (ISO 6144)*

EN ISO 6145-6, *Gas analysis - Preparation of calibration gas mixtures using dynamic methods - Part 6: Critical flow orifices (ISO 6145-6)*

EN ISO 6145-7, *Gas analysis - Preparation of calibration gas mixtures using dynamic methods - Part 7: Thermal mass-flow controllers (ISO 6145-7)*

EN ISO 6145-10, *Gas analysis - Preparation of calibration gas mixtures using dynamic volumetric methods - Part 10: Permeation method (ISO 6145-10)*

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

ISO 19229, *Gas analysis - Purity analysis and the treatment of purity data*

3   Terms and definitions

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

ISO and IEC maintain terminological 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
adjustment
adjustment of a measuring system
set of operations carried out on a measuring system so that it provides prescribed indications corresponding to given values of a quantity to be measured

Note 1 to entry: Types of adjustment of a measuring system include zero adjustment of a measuring system, offset adjustment, and span adjustment (sometimes called gain adjustment).

Note 2 to entry: Adjustment of a measuring system should not be confused with calibration, which is a prerequisite for adjustment.

Note 3 to entry: In the context of this document, adjustment is generally performed on measurement data rather than on the analyser.

[SOURCE: JCGM 200:2012, 3.11 [2]]

3.2
ambient air
outdoor air in the troposphere, excluding workplaces as defined by Directive 89/654/EEC, where provisions concerning health and safety at work apply and to which members of the public do not have regular access

[SOURCE: Council Directive 2008/50/EC [1]]

3.3
analyser
measuring system that provides an output signal which is a function of the concentration, partial pressure, flow or temperature of one or more components of a gas mixture

3.4
availability of the analyser
fraction of the time period for which valid measuring data of the ambient air concentration is available from an analyser

3.5
calibration
operation that, under specified conditions, in a first step, establishes a relation between the quantity values with measurement uncertainties provided by measurement standards and corresponding indications with associated measurement uncertainties and, in a second step, uses this information to establish a relation for obtaining a measurement result from an indication

Note 1 to entry: A calibration may be expressed by a statement, calibration function, calibration diagram, calibration curve, or calibration table. In some cases, it may consist of an additive or multiplicative correction of the indication with associated measurement uncertainty.

Note 2 to entry: Calibration should not be confused with adjustment of a measuring system, often mistakenly called "self-calibration", nor with verification of a calibration.

Note 3 to entry: Often, the first step alone in the above definition is perceived as being calibration.

prEN 14212:2022 (E)

Note 4 to entry: In the context of this document, calibration is a comparison of the analyser response to a known gas concentration with a known uncertainty when the information obtained from the comparison is used for the successive adjustment (if needed) of the analyser.

[SOURCE: JCGM 200:2012, 2.39 [2]]

3.6
certification range
concentration range for which the analyser is type tested

3.7
check
verification that the analyser is still operating within specified performance limits

3.8
combined standard uncertainty
standard uncertainty of the result of a measurement when that result is obtained from the values of a number of other quantities, equal to the positive square root of a sum of terms, the terms being the variances or co-variances of these other quantities weighted according to how the measurement result varies with changes in these quantities

[SOURCE: JCGM 100:2008, 2.3.4 [3]]

3.9
coverage factor
numerical factor used as a multiplier of the combined standard uncertainty in order to obtain an expanded uncertainty

[SOURCE: JCGM 100:2008, 2.3.6 [3]]

3.10
designated body
body which has been designated for a specific task (type testing and/or QA/QC activities in the field) by the competent authority in the Member States

3.11
detection limit
smallest concentration of a measurand that can be reliably detected by a specific measurement process

Note 1 to entry: The detection limit is calculated as $3,3 \times (s_z/B)$ where s_z is the standard deviation of analyser response at zero measurand concentration (see 8.4.5) and B is the slope of the calibration function [4].

3.12
expanded uncertainty
quantity defining an interval about the result of a measurement that can be expected to encompass a large fraction of the distribution of values that could reasonably be attributed to the measurand

Note 1 to entry: The fraction may be viewed as the coverage probability or level of confidence of the interval.

Note 2 to entry: To associate a specific level of confidence with the interval defined by the expanded uncertainty requires explicit or implicit assumptions regarding the probability distribution characterized by the measurement result and its combined standard uncertainty. The level of confidence that may be attributed to this interval can be known only to the extent to which such assumptions may be justified.

Note 3 to entry: For the purpose of this document, the expanded uncertainty is the combined standard uncertainty multiplied by a coverage factor k = 2 resulting in an interval with a level of confidence of 95 %.

[SOURCE: JCGM 100:2008, 2.3.5 [3]

3.13
fall time
difference between the response time (fall) and the lag time (fall)

3.14
independent measurement
individual measurement that is not influenced by a previous individual measurement by separating two individual measurements by at least four response times

Note 1 to entry: The largest value of response time (rise) and response time (fall) are intended.

3.15
individual measurement
measurement averaged over a time period equal to the response time of the analyser

Note 1 to entry: The largest value of response time (rise) and response time (fall) are intended.

Note 2 to entry: This definition differs from the meaning of the concept "individual measurement" in Directive 2008/50/EC [1].

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3.16
influence quantity
quantity that is not the measurand but that affects the result of the measurement

[SOURCE: JCGM 100:2008, B.2.10] [3]

3.17
interferent
component of the air sample, excluding the measured constituent, that affects the output signal

3.18
lack of fit
maximum deviation from the linear regression line of the average of a series of measurement results at the same concentration

3.19
lag time
time interval from the moment at which a step change of sample concentration occurs at the inlet of the analyser to the moment at which the output reading reaches a level corresponding to a predefined change of the stable output reading

3.20
limit value
level fixed on the basis of scientific knowledge, with the aim of avoiding, preventing or reducing harmful effects on human health and/or the environment as a whole, to be attained within a given period and not to be exceeded once attained

[SOURCE: Council Directive 2008/50/EC [1]]

3.21
long-term drift
difference between zero or span readings over a determined period of time (e.g. period of unattended operation)

3.22
monitoring station
enclosure located in the field in which an analyser has been installed to monitor concentrations of one or more ambient air pollutants

3.23
parallel measurement
measurement from different analysers, sampling from one and the same sampling manifold starting at the same time and ending at the same time

3.24
performance characteristic
one of the parameters assigned to equipment in order to define its performance

3.25
performance criterion
limiting quantitative numerical value assigned to a performance characteristic, to which conformance is tested

3.26
period of unattended operation
time period over which the drift complies with the performance criterion for long term drift

3.27
repeatability (of results of measurement)
closeness of the agreement between the results of successive individual measurements of sulfur dioxide carried out under the same conditions of measurement

Note 1 to entry: These conditions include:

a) the same measurement procedure;

b)   the same observer;

c)   the same analyser, used under the same conditions;

d)   at the same location;

e) repetition over a short period of time.

3.28
reproducibility under field conditions
closeness of the agreement between the results of simultaneous measurements with two analysers in ambient air carried out under the same conditions of measurement

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

a) the same measurement procedure;

b)   two identical analysers, used under the same conditions;

10

c)   at the same monitoring station;

d)   the period of unattended operation.

3.29
residence time inside the analyser
time period for the sampled air to be transported from the inlet of the analyser to the reaction chamber

3.30
residence time in the sampling system
time period for the sampled air to be transferred to the inlet of the analyser

3.31
response time
time interval from the instant at which a step change of sample concentration occurs at the inlet of the analyser to the instant at which the output reading reaches a level corresponding to a predefined change of the output reading

3.32
sampled air
part of ambient air that is transferred through the sampling inlet and sampling system for subsequent measurement

3.33
sample gas temperature
temperature of the sampled gas at the sample inlet

Note 1 to entry: The term "gas" can refer to a test gas used in type testing or to ambient air transferred to the analyser.

3.34
sampling system
assembly of components needed to transfer ambient air to the analyser

3.35
short-term drift
difference between zero or span readings at the beginning and end of a 12 h period

3.36
standard uncertainty
uncertainty of the result of a measurement expressed as a standard deviation

[SOURCE: JCGM 100:2008, 2.3.1 [3]

3.37
surrounding temperature
temperature of the air directly surrounding the analyser

3.38
total residence time
sum of the residence time in the sampling system and the residence time inside the analyser

3.39
type testing
examination of two or more analysers of the same design which are submitted by a manufacturer to a specified body including the tests necessary for approval of the design (determination of fitness for purpose of a specific device model / of an unambiguous designated analyser)

3.40
uncertainty of the measurement
parameter associated with the result of a measurement that characterises the dispersion of the values that could reasonably be attributed to the measurand

[SOURCE: JCGM 100:2008, 2.2.3] [3]

4   Abbreviated terms

AMS   automated measuring system (sometimes referred to as continuous automated measuring system (CAM))

FEP   perfluoro-ethylene-propylene

PTFE   polytetrafluoroethylene

5   Principle

5.1 General

This document describes the method for measurement of the concentrations of sulfur dioxide in ambient air by means of ultraviolet fluorescence. The requirements, the specific components of the ultraviolet fluorescence analyser and its sampling system are described. A number of performance characteristics with associated minimum performance criteria are given for the analyser. The actual values of these performance characteristics for a specific type of analyser shall be determined in a so-called type test for which procedures have been described. The type testing comprises laboratory tests and field tests. The selection of a type tested analyser for a specific measuring task in the field is based on the calculation of the expanded uncertainty of the measurement method. In this expanded uncertainty calculation, the actual values of various performance characteristics of a type tested analyser and the site-specific conditions at the monitoring station are taken into account (see Table 5). The expanded uncertainty of the method shall not exceed 15 % for fixed measurements or 25 % for indicative measurements (this is also specified in Annex I of Directive 2008/50/EC [1]). Requirements and recommendations for quality assurance and quality control are given for the measurements in the field (see 9.4).

5.2 Measuring principle

UV (ultraviolet) fluorescence is based on the emission of light by sulfur dioxide molecules excited by UV radiation when they return to their ground state:

The first reaction step is:

$$SO_2 + h\nu \rightarrow SO_2{}^*\tag{1}$$

In the second step the excited $SO_2{}^*$ molecule returns to its ground state, emitting an energy $h\nu'$ according to the reaction:

$$SO_2{}^* \rightarrow SO_2 + h\nu' \; (UV)\tag{2}$$

The intensity of the fluorescence radiation is proportional to the number of sulfur dioxide molecules in the detection volume and is therefore proportional to the concentration of sulfur dioxide.

Therefore:

F is the intensity of fluorescence radiation;

k is the factor of proportionality;

c_{SO_2} is the concentration of sulfur dioxide.

Before entering the fluorescence analyser, the air sample is passed through a filter in order to exclude interferences caused by contamination with particles.

The sampled air is scrubbed to remove any interference by aromatic hydrocarbons that may be present. A hydrocarbon scrubber device is used to achieve this.

The sampled air is then introduced into a reaction chamber, where it is irradiated by UV light in the wavelength range between 200 nm and 220 nm. The UV fluorescent light emitted in the wavelength range from 240 nm to 420 nm, is optically filtered and then converted to an electrical signal by a UV detector, for example, a photomultiplier tube.

The response of the analyser is proportional to the number of sulfur dioxide molecules in the reaction chamber. Therefore, temperature and pressure either need to be kept constant, or, if variation of these parameters occurs, the measured values need to be corrected.

The concentration of sulfur dioxide is expressed in the units provided by the calibration standard. The final results for reporting are expressed in μg/m³ using standard conversion factors (see Clause 10).

5.3 Type testing

The type test is based on the evaluation of performance characteristics determined under a prescribed series of tests. In this document, test procedures are described for the determination of the actual values of the performance characteristics for at least two analysers in a laboratory and the same analysers in the field, operated in parallel in both cases. The laboratory tests shall not include the sampling inlet, sampling system and external data acquisition system, but shall include analyser sampling line and filter. The field tests may include a sampling inlet and a sampling system. However, the influence of these components on the test results shall be minimized by proper maintenance.

The performance test shall be performed by a competent body. The evaluation for type testing of an analyser is based on the calculation of the expanded uncertainty in the measuring result based on the numerical values of the tested performance characteristics and compared with a prescribed maximum uncertainty.

The type testing of an analyser and subsequent QA and QC procedures provide evidence that the defined requirements concerning data quality laid out in Annex I of Directive 2008/50/EC [1] can be satisfied.

Appropriate experimental evidence shall be provided by:

— type tests performed under conditions of intended use of the specified method of measurement; and

— calculation of expanded uncertainty of results of measurement by reference to JCGM 100 [3].

5.4 Field operation and quality control

Prior to the installation and operation of a type-tested analyser at a monitoring station, an expanded uncertainty calculation shall be performed with the actual values of the performance, obtained during the type tests, and the site-specific conditions at that monitoring station. This calculation shall be used to demonstrate that the type-tested analyser meets the requirements for all applicable limit values under the actual conditions present at that specific monitoring station.