SLOVENSKI STANDARD
SIST EN 14212:2005

01-september-2005

?U_cj cgh̕ni bUb^Y[UʹnfU_UË¨GHUbXUfXbUʹa YhcXUʹnUʹXc`c Ub^Y¨_cbWʹbhfUWʹ^Y
ÿj Yd`cj Y[ UʹX]c_g]XUʹnʹi `ʹfUj]ʹ̕c`] bcʹnʹu cfYgWʹbWʹ

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

iTeh STANDARD PREVIEW

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

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Qualité de l'air ambiant - Méthode normalisée pour le mesurage de la concentration de soufre par fluorescence U.V.

Ta slovenski standard je istoveten z: **EN 14212:2005**

ICS:

13.040.20   Kakovost okoljskega zraka   Ambient atmospheres

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EUROPEAN STANDARD

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English version

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

Qualité de l'air ambiant - Méthode normalisée pour le mesurage de la concentration de SO2 par fluorescence UV

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

This European Standard was approved by CEN on 10 December 2004.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
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EN 14212:2005 (E)

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Foreword

This document (EN 14212:2005) has been prepared by Technical Committee CEN/TC 264 "Air quality", the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by September 2005, and conflicting national standards shall be withdrawn at the latest by September 2005.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

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1 Scope

This document specifies a continuous measurement method for the determination of the concentration of sulphur 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 approval tests. It also includes the evaluation of the suitability of an analyser for use in a specific fixed site so as to meet the Directives data quality requirements 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 from 0 $\mu g/m^3$ to 1 000 $\mu g/m^3$ sulphur dioxide. This concentration range represents the certification range for the type approval test.

NOTE 1   0 $\mu g/m^3$ to 1 000 $\mu g/m^3$ of SO_2 corresponds to 0 nmol/mol to 376 nmol/mol of SO_2.

NOTE 2   Lower ranges may be used for measurement systems applied at rural locations monitoring Ecosystems.

The method covers the determination of ambient air concentrations of sulphur dioxide in zones classified as rural areas, urban-background areas and traffic-orientated locations.

The results are expressed in $\mu g/m^3$ (at 293 K and 101,3 kPa).

When the standard is used for other purposes than the EU-directive, the range and uncertainty requirements need not apply.

2 Normative references

The following referenced documents are indispensable for the application 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.

ENV 13005, *Guide to the expression of uncertainty in measurement*

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 6142, *Gas analysis — Preparation of calibration gas mixtures — Gravimetric method*

ISO 6143, *Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures*

ISO 6144, *Gas analysis — Preparation of calibration gas mixtures — Static volumetric method*

ISO 6145 (all parts), *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods*

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3 Terms and definitions

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

3.1
ambient air
outdoor air in the troposphere, excluding workplace air[1]

3.2
sample gas temperature
temperature at the sample inlet outside the monitoring station

3.3
availability of the analyser
fraction of the total time period for which usually valid measuring data of the ambient air concentration is available from an analyser

3.4
calibration
comparison of the analyser response to a known gas concentration with a known uncertainty

3.5
certification range
concentration range for which the analyser is type approved

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3.6
combined standard uncertainty
calculation result of combining the uncertainties determined from all performance characteristics specified in this document according to the prescribed procedures given in this document

3.7
coverage factor
numerical factor used as a multiplier of the combined standard uncertainty in order to obtain an expanded uncertainty

3.8
designated body
body which has been designated for a specific task (type approval tests and/or QA/QC activities in the field) by the competent authority in the Member States

NOTE   It is recommended that the designated body is accredited for the specific task according to EN –ISO/IEC 17025.

3.9
expanded uncertainty
quantity defining an interval about the result of a measurement that may be expected to encompass a large fraction of the distribution of values that could reasonably be attributed to the measurand

NOTE   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 %

3.10
fall time
difference between the response time (fall) and the lag time (fall)

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[1] As stated in the relevant EU legislation.

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3.11
independent measurement
individual measurement that is not influenced by a previous individual measurement by separating two individual measurements by at least four response times

3.12
individual measurement
measurement averaged over a time period equal to the response time of the analyser

3.13
influence quantity
quantity that is not the measurand but that affects the result of the measurement (VIM 2.7), either an interferent influence quantity (i.e. the concentration of a substance in the air under investigation that is not the measurand), or an external influence quantity (i.e. a quantity that is not the measurand nor the concentration of a substance in the air mass under investigation)

NOTE   Examples are:
—   presence of interfering gases in the flue gas matrix (interferent influence quantity);
—   temperature of the surrounding air (external influence quantity);
—   atmospheric pressure (external influence quantity);
—   pressure of the gas sample (external influence quantity).

3.14
interference
response of the analyser to interferents

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3.15
interferent
component of the air sample, excluding the measured constituent, that effects the output signal

3.16
lack of fit
maximum deviation of the average of a series of measurements at the same concentration from the linear regression line

3.17
lag 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 10 % of the stable output reading

3.18
lag time (fall)
lag time for a negative step change

3.19
lag time (rise)
lag time for a positive step change

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

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

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3.22
monitoring station
enclosure located in the field in which an SO_2 analyser has been installed in such a way that its performance and operation comply with the prescribed requirements

3.23
parallel measurement
two measurements from different analysers, sampling from one and the same sampling manifiold 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 is within 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 the same measurand carried out under the same conditions of measurement [1]

NOTE   These conditions are called laboratory repeatability conditions and include:
- the same measurement procedure;
- -the same observer ;
- the same analyser, used under the same conditions;
- at the same location;
.   - 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   These conditions are called field reproducibility conditions and include:
- the same measurement procedure;
- two identical analysers, used under the same conditions;
- at the same monitoring station;
- the period of unattended operation.

NOTE 2   In this document the reproducibility under field conditions is expressed as a value with a level of confidence of 95 %

3.29
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 90 % of the stable output reading

3.30
response time (fall)
response time to a negative step change

NOTE   The response time (fall) is the sum of the lag time (fall) and the fall time.

3.31
response time (rise)
response time to a positive step change

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NOTE   The response time (rise) is the sum of the lag time (rise) and the rise time.

3.32
rise time
difference between the response time (rise) and the lag time (rise)

3.33
sampled air
ambient air that has been sampled through the sampling inlet and sampling system

3.34
sampling inlet
entrance to the sampling system where ambient air is collected from the atmosphere

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

[ENV 13005]

3.37
surrounding temperature
temperature of the air directly surrounding the analyser (temperature inside the monitoring station or laboratory)

3.38
type approval
decision taken by a designated body that the pattern of an analyser conforms to the requirements as laid down in this document

3.39
type approval test
examination of two or more analysers of the same pattern which are submitted by a manufacturer to a designated body including the tests necessary for approval of the pattern

3.40
uncertainty (of measurement)
parameter associated with the result of a measurement that characterises the dispersion of the values that could be attributed to the measureand

4   Symbols and abbreviated terms

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

A_a availability of the analyser;

av average concentration of the measurand during the field test;

b_{gp} sensitivity coefficient of the analyser to sample gas pressure change;

b_{gt} sensitivity coefficient of the analyser to sample gas temperature change;

b_{st} sensitivity coefficient of the analyser to surrounding air temperature change;

b_V sensitivity coefficient of the analyser to electrical voltage change;

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C	SO_2 concentration of the applied gas;
C_{P1}	average concentration of the measurements at sampling gas pressure P_1;
C_{P2}	average concentration of the measurements at sampling gas pressure P_2;
C_R	concentration of the reference standard;
C_s	concentration of site standard;
$C_{s,1}$	average concentration of the measurements at span level at the beginning of the drift period;
$C_{s,2}$	average concentration of the measurements at span level at the end of the drift period;
c_t	test gas concentration;
C_{T1}	average concentration of the measurements at sample gas temperature T_1;
C_{T2}	average concentration of the measurements at sample gas temperature T_2;
C_{V1}	average concentration reading of the measurements at voltage V_1;
C_{V2}	average concentration reading of the measurements at voltage V_2;
$C_{z,1}$	average concentration of the measurements at zero at the beginning of the drift period;
$C_{z,2}$	average concentration of the measurements at zero at the end of the drift period;
C_{const}^{av}	average of at least four independent measurements during the constant concentration period (t_c);
C_{var}^{av}	average of at least four independent measurements during the variable concentration period (t_v);
$\overline{d_f}$	average difference of parallel measurements;
$d_{f,i}$	the ith difference in a parallel measurement;
$D_{l,s}$	long-term drift at span concentration c_t ;
$D_{l,z}$	long-term drift at zero;
$D_{s,s}$	short-term drift at span level;
$D_{s,z}$	short-term drift at zero;
D_{sc}	difference sample/calibration port[e];
E_{ss}	sample system collection efficiency;
F_r	response factor in concentration units per voltage output of the analyser;
P_1	sampling gas pressure P_1;
P_2	sampling gas pressure P_2;
R_d	mean analyser response to the test gas directly sampled by the analyser;
r_f	reproducibility under field conditions;

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$r_{f,abs}$	absolute reproducibility in the field;
r_i	repeatability standard deviation;
$r_{l,ct}$	repeatability at concentration c_t;
$r_{l,z}$	repeatability at zero;
R_m	mean analyser response to the test gas via the sample manifold;
$s_{r,z}$	repeatability standard deviation at zero;
$s_{r,ct}$	repeatability standard deviation at concentration c_t;
$s_{r,f}$	reproducibility standard deviation under field conditions;
s_l	repeatability standard deviation;
T	surrounding air temperature;
T_1	sample gas temperature T_1;
T_2	sample gas temperature T_2;
t_d	relative difference between response time (rise) and response time (fall);
t_f	response time (fall);
T_l	surrounding air temperature at the laboratory (K);
$t_{n-1,\,0,05}$	two-sided Students t-factor at a confidence level of 0,05, with n-1 degrees of freedom;
t_r	response time (rise);
t_t	time period of the field test minus the time for calibration, conditioning and maintenance;
t_u	total time period with validated measuring data;
t_V	whole number of t_{S02} and t_{zero} pairs;
V_1	minimum voltage V_{min} (V) specified by the manufacturer;
V_2	maximum voltage V_{max} (V) specified by the manufacturer;
V_r	voltage obtained when the reference standard is injected;
V_s	voltage obtained when the site standard is injected;
V_z	voltage obtained when zero gas is injected;
$\overline{X}$	average of measurements;
x_1	first average of the measurements at T_l just after calibration;
x_z	average of the measurements at zero;
x_2	second average of the measurements at T_l just before calibration;
x_{ct}	average of the measurements at concentration c_t (µmol/mol);

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X_{av}	averaging effect;
x_c	average of the measurements using the calibration port;
$X_{H2O,z,ct}$	influence quantity of H_2O with concentration 19 mmol/mol;
$X_{H2S,z,ct}$	influence quantity of H_2S with concentration 10 nmol/mol;
x_i	the ith measurement;
$X_{int,ct}$	influence quantity of the interferent at concentration c_t (µmol/mol);
$X_{int,z}$	influence quantity of the interferent at zero (µmol/mol);
X_l	lack of fit (largest residual from the linear regression function);
$X_{NH3,z,ct}$	influence quantity of NH_3 with concentration 10 nmol/mol;
$X_{NO,z,ct}$	influence quantity of NO with concentration 500 nmol/mol;
$X_{NO2,z,ct}$	influence quantity of NO_2 with concentration 200 nmol/mol;
X_{Psg}	influence quantity of sampling gas pressure;
x_s	average of the measurements using the sample port (µmol/mol);
X_s	difference between the readings of two consecutive span checks;
x_T	average of the measurements at T_{min} or T_{max};
$X_{xl,z,ct}$	influence quantity of m-xylene with concentration 1 µmol/mol;
X_z	difference between the readings of the recent zero check and the most recent calibration;
$(x_{1,f})_i$	the ith measurement result of analyser 1, mathematically corrected for zero and span drift;
$(x_{2,f})_i$	the ith measurement result of analyser 2 at the same time as the measurement of analyser 1, mathematically corrected for zero and span drift;
Z_1	reading of the first zero check;
Z_2	reading of the second zero check;
ΔP_m	measured pressure drop induced by the manifold pump;
ΔR_a	change in the analyser's response due to the influence of the pressure drop induced by the manifold pump, expressed as a percentage;

5 Principle

5.1 General

This document describes the method for measurement of the concentration of sulphur 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 approval test for which procedures have been described. The type approval test comprises a laboratory and a field test. The selection of a type approved

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analyser for a specific measuring task in the field is based on the calculation of the combined expanded uncertainty of the measurement method. In this combined expanded uncertainty calculation the actual values of the various performance characteristics of a type approved analyser and the site-specific conditions at the monitoring station are taken into account. The combined expanded uncertainty of the method shall meet the requirements of the EU legislation. 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 SO_2 molecules excited by UV radiation when they return to their ground state:

The first reaction step is:

$$SO_2 + h\nu \rightarrow SO_2^*$$ (1)

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

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

The intensity of the fluorescence radiation is proportional to the number of SO_2 molecules in the detection volume and is therefore proportional to the concentration of SO_2.

Therefore:

$$F = k \times c_{SO_2}$$ (3)

where

F is the intensity of fluorescence radiation;

k is the factor of proportionality;

c_{SO_2} is the concentration of SO_2.

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 of 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 SO_2 molecules in the reaction chamber. Therefore, temperature and pressure either have to be kept constant, or, if variation of these parameters occurs, the measured values have to be corrected.

The concentration of sulphur dioxide is directly measured in volume/volume units if the analyser is calibrated using a volume/volume standard. The final results for reporting are expressed in µg/m^3 using standard conversion factors (see Clause 10).