SLOVENSKI STANDARD

SIST EN 15852:2010

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Kakovost zunanjega zraka - Standardna metoda za določevanje celotnega živega srebra v plinasti fazi

Ambient air quality - Standard method for the determination of total gaseous mercury

Außenluftbeschaffenheit - Standardisiertes Verfahren zur Bestimmung des gesamten gasförmigen Quecksilbers

Qualité de l'air ambiant - Méthode normalisée pour la détermination du mercure gazeux total

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13.040.20	Kakovost okoljskega zraka	Ambient atmospheres

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Ambient air quality - Standard method for the determination of total gaseous mercury

Qualité de l'air ambiant - Méthode normalisée pour la détermination du mercure gazeux total

Außenluftbeschaffenheit - Standardisiertes Verfahren zur Bestimmung des gesamten gasförmigen Quecksilbers

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Foreword

This document (EN 15852:2010) 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of an identical text or by endorsement, at the latest by December 2010, and conflicting national standards shall be withdrawn at the latest by December 2010.

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1 Scope

This European Standard specifies a standard method for determining total gaseous mercury (TGM) in ambient air using cold vapour atomic absorption spectrometry (CVAAS), or cold vapour atomic fluorescence spectrometry (CVAFS).

This European Standard is applicable to background sites that are in accordance with the requirements of Directive 2004/107/EC and to urban and industrial sites.

The performance characteristics of the method have been determined in comparative field validation tests carried out at four European locations: two background and two industrial sites. The method was tested for two months at each site over a period of twelve months using automated equipment currently used in Europe for determination of TGM in ambient air.

The working range of the method covers the range of ambient air concentrations from those found at background sites, typically less than 2 ng/m^3, up to those found at industrial sites where higher concentrations are expected. A maximum daily average up to 300 ng/m^3 was measured during the field trials.

Results are reported as the average mass of TGM per volume of air at 293,15 K and 101,325 kPa, measured over a specified time period, in nanograms per cubic metre.

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*

CR 14377, *Air quality — Approach to uncertainty estimation for ambient air reference measurement methods*

EN ISO 20988, *Air quality — Guidelines for estimating measurement uncertainty (ISO 20988:2007)*

ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of the trueness of a standard measurement method*

ISO 8573-1:2010, *Compressed air — Part 1: Contaminants and purity classes*

3 Terms and definitions

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

3.1
ambient air
outdoor air in the troposphere, excluding workplace air

3.2
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 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 Calibration should not be confused with adjustment of a measuring system, often mistakenly called "self-calibration", nor with verification of calibration.

NOTE 3 Often, the first step alone in the above definition is perceived as being calibration [ISO/IEC Guide 99:2007 (VIM)].

3.3
combined standard measurement uncertainty
standard measurement uncertainty that is obtained using the individual standard measurement uncertainties associated with the input quantities in a measurement model

NOTE In case of correlations of input quantities in a measurement model, covariances should also be taken into account when calculating the combined standard measurement uncertainty [ISO/IEC Guide 99:2007 (VIM)].

3.4
coverage factor
number larger than one by which a combined standard measurement uncertainty is multiplied to obtain an expanded measurement uncertainty

NOTE A coverage factor is usually symbolized k [ISO/IEC Guide 99:2007 (VIM)].

3.5
detection limit

measured quantity value for which the probability of falsely claiming the absence of a component in a material is β, given a probability α of falsely claiming its presence

NOTE IUPAC recommends default values for α and β equal to 0,05.

3.6
expanded standard measurement uncertainty
product of a combined standard measurement uncertainty and a factor larger than the number one

NOTE 1 The factor depends upon the type of probability distribution of the output quantity in a measurement model and on the selected coverage probability.

NOTE 2 The term "factor" in this definition refers to a coverage factor.

NOTE 3 Expanded measurement uncertainty is termed "overall uncertainty" in paragraph 5 of Recommendation INC-1 (1980) (see the GUM) and simply "uncertainty" in IEC documents [ISO/IEC Guide 99:2007 (VIM)].

NOTE 4 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 %.

3.7
measurement repeatability
measurement precision under a set of repeatability conditions of measurement

[ISO/IEC Guide 99:2007 (VIM)]

3.8
measurement reproducibility
measurement precision under reproducibility conditions of measurement

NOTE Relevant statistical terms are given in ISO 5725-1:1994 and ISO 5725-2:1994 [ISO/IEC Guide 99:2007 (VIM)].

3.9
measurement time
length of time over which the measurement instrumentation produces a single concentration value, during normal operation

NOTE 1 For "trap and desorb" instruments this will be the time period air is sampled across the gold trap prior to each thermal desorption cycle analysis; for direct measurement instruments this will be the time period in which the absorbance is averaged to produce a single value.

NOTE 2 Measurement times during the field trial campaign ranged from 30 s to 30 min.

3.10
measurement uncertainty
non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used

NOTE 1 Measurement uncertainty includes components arising from systematic effects, such as components associated with corrections and the assigned quantity values of measurement standards, as well as the definitional uncertainty. Sometimes estimated systematic effects are not corrected for but, instead, associated measurement uncertainty components are incorporated.

NOTE 2 The parameter may be, for example, a standard deviation called standard measurement uncertainty (or a specified multiple of it), or the half-width of an interval, having a stated coverage probability [ISO/IEC Guide 99:2007 (VIM)].

3.11
method detection limit

lowest amount of an analyte that is detectable using the method, as determined by sampling and analysis of zero gas

3.12

monitoring period
time period over which monitoring is intended to take place, defined in terms of the time and date of the start and end of the period

3.13
monitoring station (for mercury)
enclosure located in the field in which an analyser has been installed to monitor TGM concentrations

3.14
monitoring time
length of time over which monitoring is intended to take place

NOTE For example: an instrument measured TGM using a measurement time of 15 min, over a sampling time of 30 days (producing 2 880 data points). The monitoring period was from 0001 h on 1 April 2008 to 0001 h on 1 May 2008.

3.15
reference conditions
ambient temperature of 293,15 K and pressure of 101,325 kPa

3.16
repeatability condition of measurement
condition of measurement, out of a set of conditions that includes the same measurement procedure, same operators, same measuring system, same operating conditions and same location, and replicate measurements on the same or similar objects over a short period of time

NOTE 1 A condition of measurement is a repeatability condition only with respect to a specified set of repeatability conditions.

NOTE 2 In chemistry, the term "intra-serial precision condition of measurement" is sometimes used to designate this concept [ISO/IEC Guide 99:2007 (VIM)].

3.17
reproducibility condition of measurement
condition of measurement, out of a set of conditions that includes different locations, operators, measuring systems, and replicate measurements on the same or similar objects

NOTE 1 The different measuring systems may use different measurement procedures.

NOTE 2 A specification should give the conditions changed and unchanged, to the extent practical [ISO/IEC Guide 99:2007 (VIM)].

3.18
sampling inlet
entrance to the sampling system where ambient air is taken from the atmosphere

3.19
standard uncertainty
measurement uncertainty expressed as a standard deviation

[ISO/IEC Guide 99:2007 (VIM)]

3.20
total gaseous mercury
TGM
elemental mercury vapour (Hg^0) and reactive gaseous mercury, i.e. water-soluble mercury species with sufficiently high vapour pressure to exist in the gas phase

[Directive 2004/107/EC]

NOTE This definition is taken in this standard to include all gaseous mercury species.

3.21
zero gas
gas free from mercury, interfering compounds and particles

NOTE 1 Free from mercury means containing a concentration less than the method detection limit.

NOTE 2 Zero gas is used in conjunction to calibration of automatic mercury instruments. It may consist of pure nitrogen or synthetic air from a gas cylinder. Purified air from the surrounding can also be used (see instructions in user manuals).

4 Symbols and abbreviated terms

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

4.1 Symbols

A is a constant with numerical value - 8,134 46;

A_{Hg} is the atomic weight of mercury, 0,20059;

α for a given detection limit the probability of a false positive identification occurring;

B is a constant with numerical value 3 240,87;

β for a given detection limit the probability of a false negative identification occurring;

γ is the mass concentration;

γ_{amb} is the mercury concentration in a certain air volume $V(T, P)$;

$\gamma_{d,i}$ is the daily mass concentration value on day d from instrument i;

γ_{Hg} is the theoretical mass concentration of mercury vapour samples that can be collected from the mercury vapour source using a syringe;

$\gamma_{Hg, sou}$ is the mercury concentration in the source;

$\gamma_{Hg, syr}$ is the mercury concentration in the syringe;

γ_{MDL} is the method detection limit;

γ_{ref} is the mass concentration of TGM in reference air at 293,15 K and 101,325 kPa;

γ_{sam} is the mercury concentration related to a certain air temp (T_{sam}) and pressure (P_{sam});

$\bar{\gamma}$ is the mean mass concentration over all N days and across all M instruments;

$\bar{\gamma}_d$ is the mean mass concentration on day d across all M instruments;

D is a constant with numerical value 3 216 522;

δ is the estimated statistical uncertainty associated with the mercury vapour equation used;

$\delta_{d,i}$ is the deviation of instrument i from the mean mass concentration on day d;

$\bar{\delta}_i$ is the mean deviation of instrument i from the mean mass concentration over all N days;

k is the coverage factor;

η_{sam} is the sampling efficiency;

m_{air} is the mass of air under reference conditions;

m_{trap} is the mass of mercury found on the gold trap;

M is the number of parallel samplers used in a field trial;

M_{air} is the molecular weight of air, 0,029 kg/mol;

n is the number of measurements;

N is the duration of the field trial in days;

P_{Hg} is the vapour pressure of mercury;

P_{ref} is the reference pressure, 101,325 kPa;

P_{sam} is the actual pressure of the sampled air;

$q_{v,ave}$ is the average volume flow rate of ambient air through the trap during the monitoring period;

r^2 is the correlation coefficient;

r_{flow} is the flow calibration coefficient,

r_{syr} is the volume calibration coefficient;

R is the ideal gas constant, 8,314 J/K·mol;

R_{cal} is the instrumental response produced after the injection of a volume of mercury saturated gas;

R_i is the instrumental response generated from measurement i;

R_{sam} is the instrumental response following analysis of the sample;

$\overline{R}$ is the average of n $(n \geq 10)$ repeat measurements of R_i ;

R_0 is the instrumental response generated upon the injection of a zero volume of mercury saturated gas;

$\overline{R}_0$ is the average of n $(n \geq 10)$ repeat measurements of $R_{0,i}$;

$R_{0,i}$ is the instrumental response generated upon introduction of zero gas from measurement i ;

σ_i is the standard deviation of the deviation of instrument i over all N days;

σ_R is the relative standard deviation of a set of n measurements;

t is the sampling time;

T_{sam} is the actual temperature of the sampled air;

T_{sou} is the temperature of mercury source;

T_{syr} is the temperature of syringe;

T_{ref} is the reference temperature, 293,15 K;

$u_c(\gamma)$ is the relative combined standard uncertainty in the TGM concentration in ambient air;

$u_{c,i}(\gamma)$ is the relative combined standard uncertainty from instrument i ;

$u_{i,\,vol}$ is the uncertainty in the sampled volume for instrument i ;

$u_r(\gamma)$ is the relative random contribution to the uncertainty;

$u_{r,\,i}(\gamma)$ is the random contribution to the relative combined uncertainty from instrument i ;

$u_s(\gamma)$ is the relative non-random contribution to the uncertainty;

$u_{s,\,i}(\gamma)$ is the non-random contribution to the relative combined uncertainty from instrument i ;

U is the expanded uncertainty;

V_{amb} is the volume of ambient air sampled onto the trap;

$V(T,P)$ is a certain air volume;

$V_{sam}(T,P)$ is the corresponding air volume at the actual temperature T_{sam} and pressure P_{sam};

$\dot{V}_{\text{cal}}$ is the sensitivity of the analyser, determined by calibration;

$\dot{V}_{\text{cal},t=0}$ is the measured sensitivity of the instrument at time $t=0$;

$\dot{V}_{\text{cal},t=t}$ is the measured sensitivity of the instrument at time t;

$\Delta\dot{V}_{\text{cal}}$ is the drift in the sensitivity of the measuring system, over a time, t;

V_{Hg} is the volume of mercury saturated gas from within the mercury vapour source;

V_{ref} is the reference air volume;

x is the mass of mercury;

y is the measurement result;

Y is the measurand.

4.2 Abbreviations

CVAAS Cold Vapour Atomic Absorption Spectrometry

CVAFS Cold Vapour Atomic Fluorescence Spectrometry

EMEP Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air pollutants in Europe (European Monitoring and Evaluation Programme)

FEP Fluorinated ethylene propylene

IUPAC International Union of Pure and Applied Chemistry

MFC Mass flow controller

MFM Mass flow meter

ng Nanogram; 10^{-9} g

PTFE Polytetrafluoroethylene

TGM Total Gaseous Mercury

Zeeman AAS Zeeman Atomic Absorption Spectrometry

5 Principle

The methods described in this standard are automated methods that involve either:

— adsorption of TGM from a measured air volume on a gold trap, followed by thermal desorption of total mercury from the gold trap and determination as gaseous elemental mercury by CVAAS or CVAFS;

or

— direct continuous measurement of elemental mercury by Zeeman AAS.