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Emisije nepremičnih virov - Določevanje celotnega živega srebra - Avtomatski merilni sistemi

Stationary source emissions - Determination of total mercury - Automated measuring systems

Emissionen aus stationären Quellen - Bestimmung der Gesamtquecksilber-Konzentration - Automatische Messeinrichtungen

Émissions de sources fixes - Détermination de la concentration en mercure total - Systèmes de mesurage automatisés

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Emissionen aus stationären Quellen - Bestimmung der Gesamtquecksilber-Konzentration - Automatische Messeinrichtungen

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European foreword

This document (EN 14884:2022) 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of an identical text or by endorsement, at the latest by June 2023, and conflicting national standards shall be withdrawn at the latest by June 2023.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN shall not be held responsible for identifying any or all such patent rights.

This document supersedes EN 14884:2005.

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

This document has been prepared under a Standardization Request given to CEN by the European Commission and the European Free Trade Association.

Any feedback and questions on this document should be directed to the users’ national standards body. A complete listing of these bodies can be found on the CEN website.

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Introduction

This document describes the quality assurance procedures related to automated measuring systems (AMS) for the determination of total mercury in waste gas, in order to meet the uncertainty requirements on measured values given by regulations, e.g. EU Directives [1], national or other legislation.

This document is derived from EN 14181, which specifies general procedures for establishing quality assurance levels (QAL) for AMS installed on industrial plants for the determination of the flue gas components and other flue gas parameters. It amends EN 14181 and provides guidance specific to total mercury measurements. It is only applicable in conjunction with EN 14181.

The calibration and validation of mercury AMS that measure the total vapour phase mercury content is based on parallel measurements with the manual method described in EN 13211. The species of mercury (elemental Hg^0 and oxidized Hg^{2+}) and the physical occurrence (gaseous, dust-bound or within droplets) can vary significantly depending on the type of process to be monitored and this is taken into account when implementing the SRM.

1 Scope

This document specifies requirements for the calibration and validation (QAL2), the ongoing quality assurance during operation (QAL3) and the annual surveillance test (AST) of AMS used for monitoring total mercury emissions from stationary sources to demonstrate compliance with an emission limit value (ELV). This document is derived from EN 14181 and is only applicable in conjunction with EN 14181.

This document is applicable by direct correlation with the standard reference method (SRM) described in EN 13211.

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 13211, *Air quality — Stationary source emissions — Manual method of determination of the concentration of total mercury*

EN 14181:2014, *Stationary source emissions — Quality assurance of automated measuring systems*

EN 17255-1, *Stationary source emissions — Data acquisition and handling systems — Part 1: Specification of requirements for the handling and reporting of data*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 13211 and EN 14181 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/

4 Symbols and abbreviations

4.1 Symbols

a	intercept of the calibration function
$\hat{a}$	best estimate of a
b	slope of the calibration function
$\hat{b}$	best estimate of b
D_i	difference between SRM value, y_i and calibrated AMS value $\hat{y}_i$
$\bar{D}$	average of D_i
E	emission limit value
h	water vapour content (by volume)
i	counter
N	number of paired samples in parallel measurements
k_v	test value for variability

o oxygen content in dry gas (by volume)

o_s oxygen reference value

p gauge pressure

P percentage

s_D standard deviation of the differences D_i in parallel measurements

t Celsius temperature

t_{90} response time

t_{cycle} total measurement cycle time of AMS with pre-concentration

t_{sample} sample period of AMS with pre-concentration

U_{max} maximum permissible expanded uncertainty

x_i i^{th} AMS measured signal at AMS measuring conditions

$\bar{x}$ average of AMS measured signals

y_i i^{th} SRM measured value

$\bar{y}$ average of SRM measured values

$y_{i,\text{s}}$ i^{th} SRM measured value at standard conditions

y_{s} SRM measured value at standard conditions

$y_{\text{s,min}}$ lowest SRM measured value at standard conditions

$y_{\text{s,max}}$ highest SRM measured value at standard conditions

$\hat{y}_i$ best estimate for the "true value", calculated from the AMS measured signal x_i by means of the calibration function

$\hat{y}_{i,\text{s}}$ best estimate for the "true value", calculated from the AMS measured signal x_i by means of the calibration function at standard conditions

Δy_{max} difference between the maximum and minimum SRM measured value at standard conditions

Z_{i} check value Grubbs-Test

Z_{crit} critical limit – Grubbs-Test

σ_0 standard deviation associated with the uncertainty derived from requirements of legislation

4.2 Abbreviations

AMS automated measuring system

AST annual surveillance test

DAHS data acquisition and handling system

ELV emission limit value

QAL quality assurance level

QAL1 first quality assurance level

QAL2 second quality assurance level

QAL3 third quality assurance level

SRM standard reference method

5 Principle

The AMS measures total gaseous mercury, both elemental and oxidized, requiring a converter to reduce oxidized Hg into elemental Hg prior to measurement of total Hg. Mercury compounds are reactive and can be adsorbed onto particulate deposits within the sampling system. Therefore, the sample is often diluted with nitrogen or air in order to aid sample transport and reduce cross-interferences from other gas components within the flue gas matrix. The Hg AMS are capable of measuring the total concentration in µg/m^3 and reporting the undiluted vapour phase Hg, regardless of speciation. The sampling system is heated in order to minimize mercury chloride adsorption.

NOTE AMS often report Hg concentration on a wet basis, i.e. the water vapour from the process sample is retained within the sample. The water content is then required in order to correct the Hg concentration to dry reference conditions. If the water content is not measured by any of the installed AMS, the use of a calculated water content is acceptable as described in CEN/TS 17286 [2].

The general principles of quality assurance of AMS are laid down in EN 14181. These are applied within this standard with the amendments specific to mercury AMS being specified in the subsequent Clauses.

In this context, an AMS is any system that continuously samples the mercury content of flue gas. This may be a system that continuously analyses for mercury, typically producing a one-minute average concentration that is based on discrete or time-integrated data sampling. Alternatively, this may be a system that pre-concentrates the mercury in the flue gas, prior to analysis, within a gold accumulator for example, with a measurement cycle of typically 2 to 10 min duration. Dual accumulators are then typically used to provide continuous sampling and analysis.

Long-term sampling systems involve continuous, repetitive flue gas sampling using paired sorbent traps, located within the flue gas duct, for mercury capture, with subsequent trap analysis of the time-integrated samples. Long term sampling is typically from one day to two weeks sampling duration. The type testing, functional tests and general quality assurance requirements, applicable to long-term sampling systems, are specified in CEN/TS 17286 [2]. However, these systems also require QAL2 calibration according to EN 14181 and this standard, except for the functional tests (EN 14181:2014, 6.2 and 8.2). Alternative functional tests and quality assurance procedures are specified in CEN/TS 17286 [2].

6 Calibration and validation of the AMS (QAL2)

6.1 General

The AMS shall be calibrated and validated in accordance with EN 14181 with the modifications specified in 6.2 to 6.8 of this standard. Unless otherwise specified by regulation, the maximum permissible uncertainty is specified as 40 % of the daily ELV. EN 14181 specifies that the daily ELV, is used for quality assurance purposes.

However, for mercury a lower long term ELV, e.g. an annual ELV, may be specified. If this long term ELV is less than 50 % of the daily ELV, then the long-term ELV shall be used instead of the daily ELV, for all quality assurance assessments. However, a multiple of the longer term ELV may be used for quality assurance purposes if this is agreed with the competent authority, for example, if this is required due to more variable mercury emissions during QAL2 testing.

NOTE Annex A shows an example of the application of QAL2 for an AMS.

6.2 Functional test

6.2.1 General

Functional tests are performed to ensure that the AMS is working according to the specifications and to check the active measurement components of the AMS to ensure that they are not unduly influenced by contamination. The functional tests shall be carried out in accordance with EN 14181:2014, Annex A, with the modifications specified below. Both elemental and oxidized reference materials may be used for the functional tests, noting that only oxidized reference material (e.g. $HgCl_2$) is used for the converter efficiency test. The manufacturers' operating instructions for the reference material generators shall be followed, ensuring that a sufficient flow of reference material is used to avoid simultaneous entrainment of flue gas into the probe. The uncertainty of the reference materials shall be assessed and reported by the test laboratory. The functional test shall be performed by an experienced testing laboratory, which has been recognized by the competent authority. The independent reference material generators shall be traceable to national standards.

NOTE Protocols for the certification of both elemental and oxidized mercury generators are under development within the 'European Metrology Programme for Innovation and Research (EMPIR) project 19NRM03 SI-Hg'. This project is also assessing the stability of mercury containing solutions that are used within the generators. Until further guidance can be provided, these aspects continue to be addressed by the quality assurance procedures of the accredited test laboratory. Analytical traceability is normally established using certified reference materials such as NIST 3133 and NIST 3177.

All functional tests shall be performed by passing gaseous reference material through the entire AMS, including the filter, dilution system (if applicable), sample line, and the oxidized mercury conversion system. In the case of older AMS, when it is not possible to introduce reference material upstream of the sample filter, then elements of the sampling system may need to be bypassed in which case the test laboratory shall report a non-conformance with this document.

In the case of oxidized mercury, a reference material containing water vapour is typically specified in order to minimize mercury losses and hold-up within the sampling system. Care should be taken to volume correct the reference mercury concentration to take account of the injected water vapour concentration which should ideally be held constant. If mercury chloride solutions are used within an oxidized mercury generator supplied by the test laboratory then the stability of those solutions should be checked by the test laboratory.

6.2.2 Zero and span check (EN 14181:2014, A.7)

Elemental mercury shall be used for the independent span check provided that the reference material generator used by the test laboratory is calibrated with metrological traceability to the SI units.

NOTE Calibration according to EN ISO 17025 [3] demonstrates traceability to SI units.

Zero and span checks shall be performed by passing gaseous reference material through the entire AMS. The selected span concentration shall be no higher than 200 % of the daily ELV. The difference between the measured span result and the span gas concentration shall be ≤ 5,0 % of the daily ELV. If the first span check is outside of this tolerance then the AMS shall be adjusted according to the span adjustment procedure and re-tested. The results of these adjustments shall be reported by the test laboratory.

If the zero point is used to establish the calibration function according to EN 14181:2014, 6.4.3, procedure b), or procedure c), the zero test shall be used to prove that the AMS gives a reading at or below detection limit (as demonstrated in QAL1) at a zero concentration. The test results shall be presented in the QAL2 calibration report.