
Kakovost zraka – Emisije nepremičnih virov – Določevanje celotnega živega srebra: avtomatski merilniki

Air quality - Stationary source emissions - Determination of total mercury:
Automated measuring systems

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Foreword

This document (prEN 14884:2004) 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.

Introduction

This European Standard describes the quality assurance procedures related to Automated Measuring Systems (AMS) for the determination of total mercury in flue gas, in order to facilitate the uncertainty requirements on measured values given by regulations, national legislation or other.

This Standard is in line with the general document on quality assurance of AMS described in prEN 14181, and gives:

- requirements for the location and calibration of mercury AMS (QAL 2);
- requirements for the ongoing quality assurance during operation (QAL 3), and for the annual surveillance test (AST);
- a description of the main available principles of mercury AMS, their advantages, drawbacks and performance characteristics.

Requirements for performance characteristics (QAL 1) are not in this standard

The calibration and validation of mercury AMS are performed by parallel measurements with the reference manual method described in EN 13211. Although mercury is mainly present as metallic gaseous mercury (Hg^0) it can also be transformed in the dust phase and droplets (Hg^{2+}). A total mercury AMS or a gaseous mercury AMS can be chosen. Whether or not a gaseous mercury AMS can fulfil the requirements for total mercury depends on the process and sampling location.

1 Scope

This European Standard specifies conditions and criteria for the choice, installation and calibration of automated measuring systems (AMS) used for the monitoring of total mercury concentrations from 0,001 mg/m³ to 0,5 mg/m³ ¹⁾ (standard conditions) in exhaust gases from the incineration of waste. The method may be applicable for exhaust gases from other sources with the following typical composition:

total suspended matter	from 0 mg/m ³ to 20 mg/m ³ ;
C _x H _y	from 0 mg/m ³ to 10 mg/m ³ ;
HCl	from 0 mg/m ³ to 50 mg/m ³ ;
HF	from 0 mg/m ³ to 10 mg/m ³ ;
SO ₂	from 0 mg/m ³ to 250 mg/m ³ ;
CO	from 0 mg/m ³ to 250 mg/m ³ ;
NO _x	from 0 mg/m ³ to 500 mg/m ³ ;
CO ₂	from 0 % (volume fraction) to 15 % (volume fraction) (actual);
H ₂ O (g)	from 2 % (volume fraction) to 25 % (volume fraction) (actual) ;
O ₂	from 8 % (volume fraction) to 15 % (volume fraction) (dry, actual);
temperature	from 60 °C to 140 °C.

This European Standard is applicable on a site-specific basis by direct correlation with the manual reference method described in EN 13211.

This European Standard is primarily developed and validated for emissions from waste incinerators. From a technical point of view, it may be applied to other processes. This standard is derived from the general document on the quality assurance of AMS, prEN 14181, and shall be applied in conjunction with that document.

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2 Normative references

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This standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

ISO 9169, *Air quality — Definition and quantification of performance characteristics of measuring systems under predetermined and imposed test conditions.*

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

prEN 14181, *Stationary source emissions — Quality assurance of automated measuring systems.*

EN-ISO 14956, *Air quality — Evaluation of the suitability of a measurement method by comparison with a stated measurement uncertainty.*

EN-ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories.*

¹⁾ m³ expressed as m³ under dry conditions, normalized to 273 K and 101,3 kPa and 11,0 % (volume fraction) O₂ (unless otherwise stated).

3 Terms and definitions

For the purposes of this European Standard, the terms and definitions given in EN 13211 and prEN 14181 and the following apply.

3.1

automated measuring system (AMS)

measuring system permanently installed on site for continuous monitoring (an AMS is a secondary method which is traceable to a reference method) [prEN 14181]

3.2

cross sensitivity

response of the AMS to determinants other than mercury

3.3

linearity

capacity of a measurement method, within certain limits, to provide an instrument response or results proportional to the quantity of measurand to be determined in the sample

This proportionality is expressed through a defined a priori mathematical expression.

The linearity limits are the concentration limits in the experiment between which a linear calibration model can be applied with a known level of confidence.

NOTE It relates to the parameter measured by the instrument.

3.4

limit value

mercury concentration which is permitted by EU-legislation (or national authorities) for the plant process (i.e. average limit value). For purposes other than regulatory uses the measurement value shall be compared to a stated reference value.

3.5

overall blank

test sample taken at the plant site in an identical manner to the normal samples in the series, except that no gas is sampled during test duration

3.6

span reading

instrument reading of the AMS obtained on application of reference material [prEN 14181]

3.7

span reference material for QAL 3 purpose

simulation of the input parameter measured by the instrument at a fixed elevated mercury concentration

3.8

standard conditions

reference values for a dry gas at a pressure of 101,3 kPa and a temperature of 273 K

3.9

t_{sample}

sample time period of the automated measurement system

3.10

t_{cycle}

total measurement time of the monitor

3.11

zero reading

instrument reading of the AMS obtained on application of zero reference material [prEN 14181]

3.12

zero reference material for QAL 3 purpose

simulation of the input parameter measured by the instrument at zero mercury concentration

4 Principle

According to prEN 14181, three different levels of quality assurance are defined, designated as Quality Assurance Levels (QALs). These levels cover the suitability of an AMS for its measuring task (e.g. before or during the purchase period) of the AMS, the validation of the AMS following its installation, and the control of the AMS during its ongoing operation on an industrial plant. An Annual Surveillance Test (AST) is also defined.

The three quality assurance levels and the Annual Surveillance Test may be summarised:

QAL 1: The suitability evaluation of the AMS and its measuring procedure

In this procedure the suitability of the AMS and its measurement procedure are evaluated to assess conformance with the uncertainty requirements of the measured values. This is done by means of a total uncertainty calculation determined from all the uncertainty components arising from the individual performance characteristics. This suitability evaluation guarantees, in principle, to the operator of an installation that an AMS is able to fulfil the requirements of a stated uncertainty. The QAL 1 procedure is laid down in EN-ISO 14956.

QAL 2: Quality assurance of installation

This describes the procedures for the validation and calibration of an AMS after its installation on an industrial stack or flue gas duct. Within QAL 2 a number of parallel measurements are performed with the manual standard reference method (SRM) described in EN 13211. From the results of these parallel measurements a calibration function is established for the AMS and the uncertainties of the measured values obtained within the AMS are then evaluated against the required uncertainty.

QAL 3: Ongoing quality assurance during operation

In this level, procedures are given to demonstrate that the AMS is in control during operation so that it continues to function within the required uncertainty. This is achieved by periodic zero and span checks to the AMS and then evaluating the results obtained using control charts. Zero and span adjustments, or maintenance of the AMS, may be necessary depending on the results of this evaluation.

AST: Annual surveillance test

During the annual surveillance test the validity of the measured values obtained with the AMS is checked by means of a series of functional tests as well as by the performance of a limited number of parallel measurements using an appropriate SRM. This procedure is used to evaluate whether the measured values obtained from the AMS are still within the required uncertainty – as demonstrated in the previous QAL 2 test. It also tests whether the calibration function obtained during the previous QAL 2 test is still valid.

5 AMS performance criteria for QAL 1

The supplier shall deliver an AMS proven to be suitable for its measuring task, taking into account the specific parameter and composition of flue gas. It shall be proven that the total uncertainty of the AMS complies with the required measurement quality.

The relevant performance characteristics of the AMS shall be determined by suitability tests performed according to ISO 9169, in order to allow the calculation of the total uncertainty according to EN-ISO 14956.

These tests are usually performed in the framework of certification or type approval procedures, and the delivered AMS is assumed to have the same characteristics as the tested devices.

During QAL 1, the zero reference material and the span reference material shall be shown to be appropriate to fulfil QAL 3.

At least the following performance characteristics shall be documented:

- response time, linearity, detection limit, repeatability;
- zero and span drift;
- cross sensitivity;
- effect of temperature, electrical supply, vibration;
- effect of ambient light if relevant;
- effect of optical alignment if relevant;
- availability, maintenance interval.

In the event that the AMS does not achieve the required measurement quality, it shall not proceed forward to QAL 2 or QAL 3.

6 Mercury monitors location

The mercury monitor shall be located in such a way that the gas sample, which is monitored, has a representative content of total mercury.

NOTE The location should be chosen according to the manufacturer recommendations, and may depend on the AMS principle of detection.

The AMS shall be located to ensure that there is minimum interference with the SRM and vice versa.

The working platform(s) shall provide an easy and safe access to the AMS, to allow frequent inspection and quality assurance procedure implementation.

7 QAL 2

7.1 General

7.1.1 Calibration under operation condition

To ensure that the calibration function is valid for the range of conditions within which the plant operates, the concentration during the calibration shall be varied as much as possible within the normal operation of the plant. The concentration of mercury shall not be increased during calibration by non-operational means, such as reducing the efficiency of flue gas cleaning systems, unless it has been proven by QAL 1 that the AMS is independent to the process characteristics, which would be changed.

If clear and distinct operating modes in the plant process are included in the normal operation of the plant, such as changes in the fuel, it may be necessary to perform a calibration (and establishing a calibration

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function) for each operational mode. In this case, the monitoring system shall have a possibility to change calibration function, either in the monitor itself, or in the attached data processing system. For each calibration function (for each operating mode) the test for variability shall be performed as to 7.3.

NOTE It is recommended to perform a preliminary test to evaluate if a full calibration over the whole concentration range can be performed. Otherwise an expert can judge, based on his experience, if it is reasonable to make only one calibration covering normal changes in the process.

The results obtained from the SRM shall be expressed in the same conditions as the uncorrected results obtained from the AMS.

Calculations from concentration in operating conditions to standard conditions, and reference oxygen concentration, may be done in the monitor, but the calibration shall always be done to uncorrected operating condition.

Each SRM sample should be obtained during a period in which the conditions of the plant are as stable as possible.

7.1.2 Calibration interval

A full QAL 2 according to prEN 14181 shall be performed every three years for every AMS mercury monitor, or (if earlier) after each major change in plant operation or major changes in the set-up of the AMS mercury monitor (e.g. moving to another measuring point or changing monitor type).

This QAL 2 shall be performed and reported not later than six months after the changes.

7.1.3 Service of the AMS

The AMS mercury monitor shall be serviced just before the calibration according to the manufacturers' recommendations.

It is recommended to include the service report as appendix to the calibration report.

7.1.4 Preparation of calibration

The measurements to establish the calibration function shall be performed according to EN 13211.

The planning of the calibration measurements shall ensure that the concentration during the tests varies as much as possible within the normal operation of the plant.

7.2 Calibration procedure

7.2.1 General

The standard reference method (SRM) used shall be in accordance with EN 13211.

Calculation of the calibration function shall be based on minimum 15 valid measurements spread over at least three days and over the measuring days, normally 8 h — 10 h, aiming at having the minimum 15 valid measuring points uniformly distributed over the achieved calibration range.

In the case where all measurements are below 30 % of an emission limit level, the number of measurements may be reduced, but not to less than five measurements over three days, provided the total extraction time is maintained at a total of 7,5 h (which is equal to 15 times 30 min).

A measurement set (SRM-result and AMS reading) is valid if the AMS measurement time, excluding reading below zero or more than 100 %, internal checks or any time of malfunction, is larger than 90 % of the SRM extraction time.

Furthermore, when rinsing is required to recover the mercury deposits upstream of the filter of the sampling equipment (see 7.6.5 of EN 13211), rinsing shall be performed after each test (SRM-result and AMS reading).

The calculations for the calibration function and for the variability test shall be performed according to prEN 14181.

7.2.2 Automatic recording of output data from the AMS mercury monitor

7.2.2.1 General

During extraction of samples from the duct gas, the signal from the AMS mercury monitor shall be automatically recorded. This data shall be averaged over the same period in time, that the extraction took place.

The time difference of starting and stopping recording of the AMS mercury monitor reading shall not differ more than 30 s from the starting and stopping of the duct gas extraction.

The AMS mercury monitor may be set up to give data out digitally (e.g. via RS232) to be collected, with time stamp, in a computer, to be averaged and used for calibration function later on.

Data logging intervals and averaging times shall be reported specifically in the measurement report.

Logging of AMS mercury monitor output only on strip chart recorder, for later manual averaging ("eyeballing") is not recommended.

If the AMS mercury monitor reading is collected as electric signals, e.g. mA, the AMS mercury monitor shall be configured to give an electric signal sufficiently high, to gather the readings with reasonable accuracy. This is accepted to be fulfilled, if the majority of the readings during calibration is between 30 % and 80 % of full scale.

If it is proven that calibration curves do not change by switching from one range on the AMS to another, it may be calibrated in one range and use afterwards in another. This test and conclusion shall be clearly stated in the service report, and the service report shall in this case be part of the calibration report.

Where possible, measures to prevent the self-check during duct gas sample extraction shall be considered, e.g. by provoking a self check to finish just before starting the SRM measurements.

7.2.2.2 Continuous AMS

The AMS intrinsic average time shall not exceed 1 min during calibration. If data are recorded by sampling, the AMS intrinsic average time shall be at least twice the time period between sampling.

7.2.2.3 Discontinuous AMS

Discontinuous AMS are characterized with a total measurement cycle of monitor, t_{cycle} , and a sample time period, t_{sample} . The ratio $t_{\text{sample}} / t_{\text{cycle}}$ should be larger than 90 % in accordance with the measurement set as defined in 7.2.1.

The ratio $t_{\text{sample}} / t_{\text{cycle}}$ could be lower than 90 % in applications where there is no important and fast change in value of the mercury concentration. These situations shall be judged and approved with an expert and the variability test will also be approved, or not, if a discontinuous AMS can be used.

Also, SRM parallel measurement shall start at the beginning of a new AMS total measurement cycle and shall be performed during a discrete number of measurement cycles.

It is also important to maintain the AMS in normal operation conditions during calibration. The total duration of the measurement cycle and the sample time period shall not be modified.

If modification in monitoring cycle takes place than recalibrate.

7.3 Calibration function of the AMS mercury monitor

7.3.1 General

The user has the choice to use a normal calibration curve (as specified in 7.3.2) or a zero point calibration curve (as specified in 7.3.3) provided the variability test conditions are met.

7.3.2 Normal calibration curve and range

The calibration function is generally the least square linear regression of the measurements, to be expressed as:

$$y_i = \alpha + \beta x_i \quad (1)$$

where:

y_i is the i^{th} result of the SRM; $i = 1$ to N ; $N \geq 5$;

x_i is the i^{th} result of the AMS output; $i = 1$ to N ; $N \geq 5$;

α is the intercept of the calibration function;

β is the slope of the calibration function

Each measuring result from the AMS mercury monitor shall be converted to a calibrate value, y , by means of the above calibration function.

NOTE y is the calibrated result of the AMS mercury monitor. Sometimes a required uncertainty should be subtracted from a measurement result before comparison with an emission limit value. That procedure is outside the scope of this standard. The calibrated result of the AMS dust monitor, Y , is without subtraction of such a required uncertainty.

The normal calibration function is only valid during the operation of the plant in the range from the lowest to the highest concentration measured by the SRM during the calibration, plus an extension of 10 % of this range beyond the highest and lowest values.

7.3.3 Zero point calibration curve

For situations with variations in the concentrations during the calibration less than 15 % of emission limit value, the calibration range is the range from zero to $y_{\text{max}} + 10 \%$, and the calibration function may be determined as a straight line between the gravity point of the measured points, and zero point.

This method may only be used, if the AMS mercury monitor is serviced no more than three weeks prior to the completion of the calibration, and the zero and span point and the linearity is checked and documented in the service report. In this case, the service report shall be a part of the calibration report.

7.3.4 Measurements outside calibration range

For measurements outside the calibration range, the calibration curve shall be extrapolated in order to document the exceeding of the range.

When the value of the calibrated AMS mercury monitor measurement is above the defined calibration range, a new calibration function by means of parallel measurements shall be performed.

NOTE Calculating the calibration function data from previous calibrations should not be used.

The validity of the measured values obtained using the AMS shall be evaluated by the plant owner on a weekly basis (Monday to Sunday). A full new calibration (QAL 2) shall be performed, reported and implemented within 6 months, if any of the following conditions occur:

- a) > 5 % of the number of the AMS mercury monitor measured values calculated over a weekly period (based on calibrated values and expressed in the same units as the calibration) are outside the valid calibration range for more than 5 weeks between two ASTs, and
- b) > 40 % of the number of the AMS mercury monitor measured values calculated over this weekly period (based on calibrated values and in the same units as the calibration) are outside the valid calibration range for one or more weeks.

If a plant operates above the valid calibration range but below 50 % of ELV, then the competent authority can allow the plant to perform an AST instead of the QAL 2 procedures. If the AST demonstrates that the existing calibration function is valid beyond the calibration range, the competent authority can allow the plant to extend the calibration range up to the measured concentrations (but below 50 % of ELV) determined during the AST.

Until the new calibration function has been implemented the previous calibration function may be used.

7.4 Corrections for mercury deposits in the SRM-extraction system

Validation test performed during writing of EN 13211 proved, that only a few % of total mercury collected on the sampling equipment may be lost in the extraction cone and tubes up stream of the filter.

When dust bounded mercury is sampled isokinetically according to EN 13211 as SRM to calibrate an AMS mercury monitor, rinsing of the extraction tubes shall be carried out as described in EN 13211 at each change of filter. The rinsing solution together with the particulate matter collected in the rinsing process shall be analysed on the mass of total mercury and added to the mass of total mercury collected on the filter and absorbers.

When rinsing is required (see EN 13211) this shall be carried out after the last measuring that day. Divide the Hg-mass over the number of measurements that day.

The test report shall show separately the amount of mercury collected on the filter, absorbers, and rinsing solution of the extraction system, separately for each filter.

7.5 Calculation of variability

Depending on the plant process, regulation may require a maximum uncertainty for the AMS measurement.

Convert the required uncertainty in terms to an absolute standard deviation, σ , by using the factor of 1,96 as the value for the coverage factor (see prEN 14181 for details). The conversion is obtained by this formula:

$$\sigma = \frac{x \times \text{ELV}}{100 \times 1,96} \quad (2)$$

where:

- x is the allowed maximum uncertainty of the AMS measurement at a confidence level of 95% at the emission limit value (ELV) expressed as a percentage of the ELV;
- σ is the allowed maximum standard deviation of the AMS calibration function. All data shall be transformed to standard condition to be comparable to the ELV, and the variability test shall be fulfilled at these conditions.
- ELV is the Emission Limit Value.