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Kakovost zunanjega zraka - Standardna metoda za določevanje živega srebra v usedlinah

Ambient air quality - Standard method for the determination of mercury deposition

Außenluftbeschaffenheit - Standardisiertes Verfahren zur Bestimmung der Quecksilberdeposition

Qualité de l'air ambiant - Méthode normalisée pour la détermination des dépôts de mercure

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Ambient air quality - Standard method for the determination of mercury deposition

Qualité de l'air ambiant - Méthode normalisée pour la détermination des dépôts de mercure

Außenluftbeschaffenheit - Standardisiertes Verfahren zur Bestimmung der Quecksilberdeposition

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Foreword

This document (EN 15853:2010) 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of an identical text or by endorsement, at the latest by December 2010, and conflicting national standards shall be withdrawn at the latest by December 2010.

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

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association, and supports essential requirements of EU Directive(s).

There are currently only European Standard methods for the determination of the mercury concentration in water samples (EN ISO 17852, *Water quality — Determination of mercury — Method using atomic fluorescence spectrometry (ISO 17852:2006)* and EN 1483, *Water quality — Determination of mercury — Method using atomic absorption spectrometry*) but no standard method exists for the determination of mercury in precipitation, though OSPAR/EMEP reference methods are currently available for mercury in precipitation.

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

1 Scope

This European Standard specifies a method for the determination of the total deposition of mercury. This standard can be used within the framework of the European Council Directive on Ambient Air Quality Assessment and Management and Directive 2004/107/EC. Performance requirements with which the method should comply are specified in this European Standard. The performance characteristics of the method were determined in comparative field validation tests carried out at two European locations.

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.

This standard allows the sampling of deposition using cylindrical deposition gauges, and analysis using Cold Vapour Atomic Absorption Spectrometry (CVAAS) or Cold Vapour Atomic Fluorescence Spectrometry (CVAFS) following existing harmonised and standardised procedures. The standard is applicable for the measurement of mercury in deposition between 1 ng/(m^2·d) and 100 ng/(m^2·d).

The standard is validated for the deposition range listed in Table 1.

Table 1 — Working range of this standard method

Working range ng/(m^2·d)	
Lower limit	Upper limit
1	100

NOTE The range given is based upon the values measured in the field validation test. The upper and lower limits are the observed minimum and maximum values measured during the field validation tests. The actual lower limits of the working range depends on the variability of the laboratory blank, for bulk and wet-only collectors, and the precipitation. The method can be applied to higher and lower deposition rates provided that the collection characteristics are not compromised.

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 17852, *Water quality — Determination of mercury — Method using atomic fluorescence spectrometry (ISO 17852:2006)*

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

3 Terms, definitions and abbreviations

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

3.1 Terms and definitions

3.1.1
ambient air
outdoor air in the troposphere, excluding workplace air

3.1.2
atmospheric deposition
mass flow rate (unit of mass per unit of area per unit of time) describing the process of the transfer of any species from the atmosphere to an environmental compartment, e.g. air to water, air to soil

NOTE Atmospheric deposition is the sum of the depositions of sedimenting particles, non-sedimenting particles and gases.

3.1.3
bulk collector
equipment to collect bulk deposition

NOTE Bulk collectors sample deposition at all times. A bulk sampler can consist of a funnel-bottle combination or a wide mouthed jar.

3.1.4
bulk deposition
sum of the deposition of sedimenting wet and dry particles

NOTE Bulk deposition is a part of the atmospheric deposition.

3.1.5
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 (VIM)].

3.1.6
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 (VIM)].

3.1.7
detection limit (DL), instrumental
lowest amount of an analyte that is detectable using an instrument as determined by repeated measurements of a reagent blank

3.1.8
detection limit (DL), method
lowest amount of an analyte detectable after the whole measurement process as determined by repeated measurements of different field blanks

3.1.9
dry deposition
sum of the deposition of sedimenting dry particles, non sedimenting particles and gases

NOTE Dry deposition includes the following processes: atmospheric turbulent diffusion, adsorption, absorption, impaction and gravitational settling. The dry deposition process is affected by the type of underlying surface and surface conditions. Dry deposition is a part of the atmospheric deposition.

3.1.10
expanded 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 (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 %.

3.1.11
field blank

artificial sample (e.g. de-ionised water) taken through the same procedure as the precipitation sample, except that this has not been exposed to precipitation

NOTE It is transported to the sampling site, mounted in the sampling unit, returned to the laboratory and worked up in the same way as the deposition sample.

3.1.12
laboratory blank

artificial sample (e.g. de-ionised water) taken through the same procedure in the laboratory as the precipitation sample, worked up in the same way as the deposition sample

3.1.13
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)]

3.1.14
precipitation

rain, snow, sleet, snow pellets ("graupel") and hail

3.1.15
reagent blank

artificial sample (e.g. de-ionised water) processed through the analytical measurement steps

3.1.16
wet deposition

sum of depositions of sedimenting wet particles and droplets

NOTE Wet particles and droplets in the atmosphere undergo the process of scavenging of any gases and/or particles. Wet deposition is a part of the atmospheric deposition.

3.1.17
wet-only collector

equipment to collect wet deposition, typically a funnel-bottle combination

NOTE Wet-only collectors collect only during wet precipitation events

3.2 Abbreviations

CRM	Certified Reference Material
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)
WMO/GAW	World Meteorological Organization/Global Atmosphere Watch

4 Principle of mercury deposition determinations

Atmospheric deposition is defined as the sum of the depositions of sedimenting particles, non-sedimenting particles and gases. Total atmospheric deposition is the sum of dry deposition and wet deposition. Bulk deposition is the sedimenting part of the atmospheric deposition.

There is no method available to determine total atmospheric deposition in one measurement. The determination of the dry deposition requires micrometeorological measurements, taking into account the turbulent atmospheric transport processes. Wet deposition and bulk deposition, however, can be estimated using suitable collectors.

This standard describes methods to determine wet deposition and bulk deposition of mercury using wet-only- and bulk collectors.

The wet-only collector is designed to collect sedimenting water containing wet particles only, while the bulk collector is designed to collect all sedimenting wet and dry particles. However, since the deposition process is affected by various factors, e.g. wind speed, temperature, vegetation, surface type, etc., the wet-only collector will not catch all sedimenting wet particles while some sedimenting dry particles, non-sedimenting particles and gases will be collected. Also, the bulk collector will not catch all sedimenting particles while some non-sedimenting particles and gases will be collected.

The method is divided into two main parts:

a) sampling of precipitation in the field;

b) mercury analysis in the laboratory.

The precipitation sample is stabilized with hydrochloric acid and transferred to the laboratory in the collection vessel. Mercury in the precipitation sample is oxidised using bromine monochloride. Mercury is analysed either by CVAAS or CVAFS detection.

5 Siting requirements for mercury deposition determinations

The following guidelines shall be met as far as practicable (Annex III.II of Directive 2004/107/EC [10]):

a) The site chosen for sampling and measurements shall be representative of a larger area. The size of this area is determined by site characteristic (urban, industrial or rural) and the variability of the air and precipitation quality.

b) The collector shall as far as possible not be exposed to areas where unrepresentative strong winds occur like shores, cliffs and top of hills, but it shall also not be sheltered by tall trees or buildings. The flow around the collector shall be unrestricted, without any obstructions affecting the airflow in the vicinity of the sampler. The criteria depend on the site characteristic:

1) Rural sites: there shall be no obstacles, such as trees, above 30° from the rim of the precipitation collector, and buildings, hedges, or topographical features which may give rise to updraughts or downdraughts. See EMEP manual [1] for details;

2) Urban and industry sites: one shall seek to meet the same requirements but shall be at least some metres away from buildings, trees and other obstacles.

c) For the deposition measurements in rural background areas, the EMEP guidelines and criteria shall be applied as far as practicable and where not provided for in the guidelines given above.

NOTE The method has not been tested at mining sites or sites with significant presence of particles containing cinnabar (HgS). At such sites the method can be applied provided that the digestion characteristics are not compromised.

6 Reagents

6.1 Concentrated hydrochloric acid, 30 % HCl or 36 to 38 % HCl (low mercury blank required, e.g. Suprapur® [1] quality).

WARNING — Concentrated hydrochloric acid is corrosive, and hydrogen chloride fumes are an irritant. Avoid exposure by contact with the skin or eyes, or by inhalation of fumes. Carry out the work in a fume cupboard. Use suitable personal protective equipment (including suitable gloves, face shield or safety glasses, etc.) when working with the concentrated or dilute hydrochloric acid.

6.2 Concentrated hydrochloric acid, 37 % HCl (e.g. p.a. quality) for cleaning purposes.

6.3 Ultrapure water, de-ionised water with a resistivity greater than 18 MΩ·cm at 25 °C.

Water shall be monitored for Hg, especially after ion exchange beds are changed.

6.4 Hydrochloric acid, 2 % HCl for cleaning purposes, prepared from concentrated HCl (6.2) by dilution with ultrapure water (6.3).

6.5 Hydrochloric acid, 2 % HCl for for acidification of the precipitation samples, prepared from concentrated HCl (6.1) by dilution with ultrapure water (6.3).

6.6 Potassium bromate ($KBrO_3$), e.g. p.a. quality; if necessary preheated overnight at (240 ± 20) °C to evaporate mercury.

WARNING — Potassium bromate can cause cancer.

6.7 Potassium bromide (KBr), e.g. Suprapur® [1] quality; if necessary preheated overnight at (240 ± 20) °C to evaporate mercury.

6.8 Bromine monochloride (BrCl) solution.

Dissolve 1,10 g $KBrO_3$ (6.6) and 1,5 g KBr (6.7) by adding to 20 ml ultrapure water (6.3) with careful shaking and heating, if necessary. Afterwards, slowly add 80 ml HCl (6.1) whilst stirring.

To avoid contamination, store in a mercury free environment.

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[1] Suprapur® is an example of a suitable product available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.

WARNING — Shall be prepared in a fume hood with great care. Use safety goggles. Large amounts of acid fumes and gaseous free halogens will form and evaporate from the solution.

6.9 Bromine monochloride (BrCl) solution, 0,5 % V/V for cleaning purposes, prepared of Bromine monochloride (BrCl) solution (6.8) by dilution with ultrapure water (6.3).

6.10 Hydroxylammonium hydrochloride solution.

Dissolve 12,0 g $NH_2OH{\cdot}HCl$ in 100 ml water (6.3). This chemical reagent sometimes contains high mercury concentrations. Adding 0,1 g Chelex 100 ion exchange material can lower the mercury content. Blanks shall be checked carefully.

NOTE Instead of hydroxylammonium hydrochloride solution ascorbic acid can be used. Ascorbic acid solution can be prepared weekly by dissolving 10 g of L-ascorbic acid in 100 ml water (6.3).

7 Sampling

7.1 Sampling equipment – General requirements

Use collectors with a defined horizontal opening, either a funnel/bottle combination (see A.1 and A.3) or a wide-mouthed jar (see A.2). The collectors can be bulk samplers, which collect at all times, or wet-only samplers which collect only during wet precipitation events.

If a funnel/bottle collector is used, the funnel shall have a cylindrical vertical section of sufficient height to avoid sampling losses resulting from splashing. If a jar is used, it shall have a sufficient depth to avoid such sampling losses.

Collector dimensions shall be selected with respect to the expected precipitation collected in the sampling period used. Typical sampling periods vary between one week and one month. The funnel area shall be large enough to provide sufficient sample for chemical analysis at a minimum precipitation depth of 1 mm per week.

It is recommended that short sampling periods (weekly) and/or two or three samplers in parallel are used.

The sampling efficiency of funnel/bottle collectors can be checked by comparing the collected precipitation with the precipitation determined using a standard meteorological rain gauge. The difference in precipitation between the standard rain gauge and the heavy metal sample collector shall not be greater than 20 % for precipitation depths between 1 mm to 2,5 mm, and not greater than 10 % for precipitation depths larger than 2,5 mm of precipitation [9]. Checking sampling efficiency is especially important if a wet-only collector is used.

Mercury deposition is collected in special precipitation samplers, which are used only for mercury deposition determinations. All parts of the precipitation collector that are in contact with the sample shall consist of materials that do not alter the mercury content of the sample (e.g. glass, fluorocarbon polymers). Also, all parts of the sampling collectors shall be easy to clean.

In order for the sample not to be contaminated during heavy rain, the rim of the funnel shall be positioned 1,5 m to 2,0 m above the ground level.

NOTE Sample contamination can be caused by insects, bird droppings or other material in the sampling vessels, especially when using extended sampling periods. This is a major drawback to bulk sampling.

For extended sampling periods − especially if HCl is used to preserve the sample during exposure − it is necessary to prevent the diffusion of Hg^0 into the precipitation sample collected, since it could contribute to the mercury content of the sample via oxidation to water-soluble forms. For funnel/bottle collectors this can be done easily by using a capillary tube between the funnel and the bottle.

It is also necessary to shield the sample bottles from light to avoid photo-induced reduction of the mercury in the precipitation sample.

If a funnel/bottle collector with capillary tube is used, add HCl (6.1 or 6.5) to the sampling bottle before exposure in order to stabilize the sample (see 7.3). Do not add acid, if an open jar is used for sampling.

Samplers shall be suitable for all seasons and all climatic conditions. Thus, especially for wet-only collectors, a heating device should be included to melt snow and to prevent the formation of ice in the funnel and bottle during winter. Otherwise, for bulk collectors, an extra large and deep cylindrical jar should be used for snow sampling. It can be useful to cool the samples in locations where high temperatures are expected during summer.

7.2 Sampling equipment − Special requirements for different collector types

7.2.1 Bulk collector: Funnel/bottle combination

Sampling equipment as described in A.1 can be used for sampling.

If a bird ring is needed, it shall be covered by a suitable inert material, e.g. polyethylene. In order to prevent insects, leaves, etc. from entering the collection bottle a sieve made of e.g. polycarbonate can be used. The sieve shall not obstruct the funnel neck.

Funnel/bottle combination bulk collectors can be used at all types of sampling sites.

7.2.2 Bulk collector: Wide-mouthed jar

Sampling equipment as described in A.2 can be used for sampling. If a bird ring is needed, it shall be covered by a suitable inert material, e.g. polyethylene.

Wide-mouthed jar bulk collectors can be used at all types of sampling sites.

7.2.3 Wet-only collector: Funnel/bottle combination

Sampling equipment as described in A.3 can be used for sampling.

Wet only collectors are equipped with an automatic lid, which opens after activation of a precipitation sensor. The sensitivity of the sensor might affect the sampling efficiency. A precipitation of 0,05 mm/h shall be sufficient for the lid opening mechanism to be activated.

Wet-only collectors can be used at all types of sampling sites.

NOTE Especially at industrial sites or at costal sites, corrosion by e.g. reactive gases or sea salts can occur to precipitation sensors based on measuring the electrical conductivity. At such sites it can be useful to use optical sensors.

7.3 Preparation of precipitation collectors

All parts of the precipitation collector that are in contact with the sample shall be cleaned extensively before use. Plastic gloves shall be used during all steps of the cleaning procedure. It is recommended to store cleaned sampling vessels in double plastic bags.

A suitable cleaning procedure is given below.

a) Wash with an alkaline detergent. Rinse thoroughly with ultrapure water;

b) Leach with 2 % HCl (6.4) for one day to two days. This can be done in a polyethylene tank. Rinse thoroughly with ultrapure water;

c) Leach contaminated labware in BrCl solution (6.9). Leave to stand for at least 24 h. Add Hydroxylammonium hydrochloride solution (6.10) to remove BrCl from the solution. Rinse thoroughly with ultrapure water.