BRITISH STANDARD

BS EN 15841:2009

Ambient air quality — Standard method for determination of arsenic, cadmium, lead and nickel in atmospheric deposition

ICS 13.040.20

British Standards

National foreword

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Ambient air quality - Standard method for determination of arsenic, cadmium, lead and nickel in atmospheric deposition

Qualité de l'air ambiant - Méthode normalisée pour la détermination des dépots d'arsenic, de cadmium, de nickel et de plomb

Luftbeschaffenheit - Messverfahren zur Bestimmung von Arsen, Kadmium, Blei and Nickel in atmosphärischer Deposition

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Foreword

This document (EN 15841:2009) 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of an identical text or by endorsement, at the latest by May 2010, and conflicting national standards shall be withdrawn at the latest by May 2010.

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For relationship with EU Directive(s), see informative Annex ZA, which is an integral part of this document.

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1 Scope

This European Standard specifies three methods for the determination of deposition of arsenic (As), cadmium (Cd) nickel (Ni) and lead (Pb), that can be used in the framework of the European Council Directive on Ambient Air Quality Assessment and Management [1] and the 4th Air Quality Daughter Directive [2]. This European Standard specifies performance requirements with which the method has to comply in order to meet the data quality objectives given in the Directives. The performance characteristics of the method were determined in comparative field validation tests carried out at four European locations [3].

This European Standard specifies methods for sampling wet-only and bulk deposition of As, Cd, Ni and Pb, sample treatment and analysis by graphite furnace atomic absorption spectrometry (GF-AAS) or by inductively coupled plasma mass spectrometry (ICP-MS).

The method is applicable for deposition measurements in

a) rural and remote areas;

b) industrial areas;

c) urban areas.

The standard is validated for the working ranges listed in Table 1.

Table 1 — Validated working ranges for the methods

	Lower limit (µg/m² day)	**Upper limit** (µg/m² day)
As	0,05	2
Cd	0,01	1
Ni	0,05	25
Pb	0,1	65

NOTE The ranges given are 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 ranges depend on the variability of the laboratory blank and the precipitation amount range in bulk and wet-only.

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.

EN 14902:2005, *Ambient air quality – Standard method for the measurement of Pb, Cd, As and Ni in the PM10 fraction of suspended particulate matter*

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

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

3 Terms, definitions and abbreviations

3.1 Terms and definitions

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

3.1.1
analysis
all operations carried out after sample preparation to determine the amount or concentration of the metals or metalloids of interest present in the sample

3.1.2
Bergerhoff collector
wide mouthed bucket mounted on a post, openly exposed at all time

3.1.3
bulk collector
funnel-bottle combination openly exposed at all time

NOTE In this standard two methods for the bulk collector are described: the “bulk bottle method” (only the liquid collected in the bottle is analysed) and the “bulk bottle+funnel method” (the liquid collected in the bottle plus the solid collected on the funnel are analysed).

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

NOTE Both bulk and Bergerhoff collectors sample bulk deposition.

3.1.5
coverage factor
numerical factor used as multiplier of the combined standard uncertainty in order to obtain an expanded uncertainty

[EN ISO 20988:2007, 3.3; ISO/IEC Guide 98:2008, 2.3.6]

3.1.6
detection limit (DL), instrumental
lowest amount of an analyte that is detectable using an instrument as determined by repeated measurements of a reagent blank

3.1.7
detection limit (DL), method
lowest amount of an analyte detectable after the whole measurement process as determined by repeated measurements of different field blanks

3.1.8
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.

3.1.9
expanded uncertainty
expanded measurement uncertainty
quantity defining an interval $\left\lfloor y - U_p(y); y + U_p(y) \right\rfloor$ about the result of a measurement that can be expected to encompass a large fraction p of the distribution of values that could reasonably be attributed to the measurand

[EN ISO 20988:2007, 3.4; ISO/IEC Guide 98:2008, 2.3.5]

3.1.10
field blank
artificial sample (e.g. de-ionised water) transported to the sampling site, mounted in the sampling unit, but not exposed to ambient air, returned to the laboratory and worked up in the same way as the deposition sample

3.1.11
laboratory blank
artificial sample (e.g. de-ionised water) worked up in the same way as the deposition sample in the laboratory

3.1.12
precipitation
rain, snow, sleet, graupel and hail

3.1.13
reagent blank
artificial sample (e.g. de-ionised water) that contains all the reagents used during analysis of the sample, but without the sample matrix

3.1.14
repeatability
closeness of the agreement between the results of successive measurements of the same measurand carried out under the same conditions of measurements

[ISO/IEC Guide 98:2008, B.2.15]

3.1.15
reproducibility
closeness of the agreement between the results of measurements of the same measurand carried out under changed conditions of measurements

[ISO/IEC Guide 98:2008, B.2.15]

3.1.16
sample digestion
sample dissolution process to obtain a solution containing the analyte of interest

3.1.17
sample preparation
all operations carried out on a sample, after transportation and storage, to prepare it for analysis, including transformation of the sample into a measurable state, where necessary

3.1.18
standard operating procedure
SOP
written set of procedures that details the method of an operation, analysis, or action whose techniques and procedures are thoroughly prescribed and that is accepted as the method for performing certain routine or repetitive tasks

3.1.19
standard uncertainty
standard measurement uncertainty
measurements uncertainty expressed as a standard deviation

[EN ISO 20988:2007, 3.18; ISO/IEC Guide 98:2008, 2.3.1]

3.1.20
uncertainty (of a measurement)
measurement uncertainty
parameter associated with the result of a measurement that characterises the dispersion of the values that could reasonably be attributed to the measurement

[EN ISO 20988:2007, 3.18; ISO/IEC Guide 98:2008, B.2.18;]

3.1.21
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.

3.1.22
wet-only collector
collector open only during precipitation events, typically a funnel-bottle combination

3.2 Abbreviations

EMEP	Co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe
GF-AAS	Graphite Furnace - Atomic Absorption Spectrometry
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
SOP	Standard Operating Procedure
CRM	Certified Reference Material
WMO/GAW	World Meteorological Organization/Global Atmosphere Watch

4 Principle

Total atmospheric deposition of metals, which is defined as the sum of the deposition of sedimenting particles, non-sedimenting particles and gases, or sum of wet and dry deposition, cannot be determined by a single simple method.

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 using wet-only and bulk collectors. The wet-only collector is designed to collect only sedimenting wet particles, 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 and surface type, 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 sample is transferred to the laboratory in the sampling bottle (wet only and bulk collector) or bucket (Bergerhoff collector). Arsenic, cadmium, nickel and lead are taken into solution by digestion techniques and analysed by appropriate analytical instruments (i.e. ICP-MS and GF-AAS) depending on deposition level to be measured.

Close to industrial sources bulk deposition of metals comprises approximately their atmospheric deposition. At background sites with high precipitation the measurement of bulk and wet deposition is shown to be equivalent.

5 Apparatus and reagents

5.1 Reagents

5.1.1 Ultrapure water distilled or deionised

It is recommended that the water used should be obtained from a water purification system that delivers ultrapure water having a resistivity of 18,2 MΩ·cm or greater at 25 °C.

5.1.2 Nitric acid (HNO_3), concentrated

Density about 1,42 g/ml, mass fraction about 70 %, high purity grade (concentration stated by the manufacturer or supplier < 0,005 mg/l for As, Cd, Ni and Pb (typical concentrations are generally ten times lower)), sub-boiled before use if necessary.

WARNING — Concentrated nitric acid is corrosive and oxidising, and nitric acid fumes are irritants. 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 nitric acid.

5.1.3 Nitric acid for cleaning purposes (2 % by volume)

Add approximately 800 ml of ultrapure water to a 1 l acid cleaned volumetric flask. Carefully add 20 ml of concentrated nitric acid to the flask and swirl to mix. Allow to cool, dilute to 1 l with ultrapure water and mix thoroughly.

5.1.4 Nitric acid for filtration purposes (1 % by volume)

Add approximately 900 ml of ultrapure water to a 1 l acid cleaned volumetric flask. Carefully add 10 ml of concentrated nitric acid (5.1.2) to the flask and swirl to mix. Allow to cool, dilute to 1 l with ultrapure water and mix thoroughly.

5.1.5 Hydrogen peroxide (H_2O_2), mass fraction about 30 %

High purity grade (concentration stated by the manufacture or supplier < 0,005 mg/l for As, Cd, Ni and Pb (typical concentration are generally ten times lower)).

5.2 Sampling equipment

5.2.1 General

Depending on site characteristics (6.1), three different types of collectors can be used to measure deposition of arsenic, cadmium, nickel and lead: wet-only (3.1.22), bulk (3.1.3) and Bergerhoff collector (3.1.2). The two first types of collectors are bottle+funnel combinations while the latter is an open bucket. The choice of which sampler to use is discussed in 6.1.

5.2.2 General requirements for sampling equipment

Collectors shall have a cylindrical vertical section of sufficient height to avoid sampling losses resulting from splashing. See Annex A for illustrations of the samplers used in the field trial.

The diameter for the opening area and the volume of the collector need to be selected to be of appropriate size to collect all the precipitation for the required sampling duration. 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 height of 1 mm per week.

In order for the sample not to be contaminated from the ground during heavy rain, the height of the opening through which precipitation enters the sampler (i.e., the collection orifice) shall be at least 1,5 m above ground. For areas that receive high snowfall accumulations, the sampler may be raised onto a platform above the snow [4].

No parts of the collector that are in contact with the sample shall be made of metal. All parts should be easily cleaned. The collector and all surfaces in contact with the samples should be inert for the analytes measured, for example high density polyethylene.

NOTE Different samplers may have different sampling efficiency, which can lead to incomparable results. The sampling efficiency for precipitation may be checked conducting parallel measurement with a standard precipitation gauge. The difference in precipitation amount between the standard rain gauge and the bulk or wet-only collectors should not be greater than 20 %.

See Annex A for examples of sampling standard operating procedures.

5.2.3 Wet-only collector

A wet-only collector is used to sample precipitation only (3.1.12). The wet-only collectors shall be open during precipitation events and be closed during dry periods. An automated wet-only collector should have the following components: a precipitation sample container (funnel+bottle combination), a lid that opens and closes over the sample container orifice, a precipitation sensor, a motorized drive mechanism with associated electronic controls, and a support structure to house the components.

It is recommended that the sampler is temperature controlled to avoid freezing and evaporation of the rain water.

The collection efficiency for a wet-only collector is dependent on the sensitivity of the sensor. The sensor should be designed with a response, which will cause the lid to open when the precipitation intensity exceeds 0,05 mm/h [5].

Samplers shall be designed for sampling during all seasons and all relevant climatic conditions. Thus, a heating device could be included for melting snow and to prevent the formation of ice in the funnel or bottle during winter.

NOTE Depending on climatic conditions, it can be useful to cool the samples in locations where high rates of evaporation are expected during summer.

5.2.4 Bulk collector

A bulk collector consists of a bottle+funnel combination openly exposed at all times (3.1.3). In order to prevent insects, leaves, etc. from entering the collection bottle use a sieve made of e.g. polycarbonate. The sieve should be free and not tied up in the funnel neck.

NOTE An extra large and deep cylindrical bucket could be used for snow sampling. This is in principle the same as a large type of Bergerhoff collector, but one should notice that the collector illustrated in A.1 is too small for proper snow sampling.

5.2.5 Bergerhoff collector sampler

A Bergerhoff collector is a bucket installed on a top of a post. Optionally this can be equipped with a bird guard.

NOTE The Bergerhoff collectors used in the field trial had a collecting volume of 1,5 l and an opening of about 100 mm in diameter.

5.3 Laboratory equipment

5.3.1 General

Ordinary laboratory apparatus and the laboratory equipment given in 5.3.2 to 5.3.5 are required.

5.3.2 Microwave digestion system

A microwave digestion system including chemical resistant vessels as described in EN 14902 shall be used for digestion of Bergerhoff samples (see 7.3) and filters (see 7.2.2). The microwave cavity shall be corrosion resistant and well ventilated, with all electronics protected against corrosion to ensure safe operation. Ensure that the manufacturer’s safety recommendations are followed.

NOTE A leakage detection or pressure control system is very useful, since it provides a safeguard against the possibility of sample loss due to excessive pressure build-up and partial venting of the sample vessels.

5.3.3 Drying device

This is either a hot plate or a furnace to evaporate the Bergerhoff samples to dryness.

5.3.4 Graphite furnace-atomic absorption spectrometer (GF-AAS)

Equipped with hollow cathode lamps or electrodeless discharge lamps for the elements of interest, capable of carrying out simultaneous background correction at the measurement wavelengths using a continuum source such as a deuterium lamp to correct for non-specific attenuation or using a Zeeman background correction system.

5.3.5 Inductively coupled plasma - mass spectrometer (ICP-MS)

Mass spectrometer (e.g. quadrupole instrument) capable of scanning the mass range from 5 u (unified atomic mass unit) to 250 u with a minimum resolution capability of 1 u peak width at 5 % peak height, equipped with a data system that allows correction of isobaric interferences and the application of the internal standard technique.

NOTE The use of alternative ICP-MS instrumental configurations, e.g. high resolution mass spectrometers, quadrupole mass spectrometers equipped with reaction or collision cells, cold plasma systems, etc., can reduce spectral interferences.

6 Sampling

6.1 Sampling strategy

Different sampling strategies are needed for rural and industrial sites. For urban areas the pollution level can be similar to rural sites, and in this case one should follow sampling strategy for rural sites. Other urban environments can be more polluted, and if so one should follow the sampling strategy for industrial sites.

At background sites (rural and less polluted urban area) with high precipitation the bulk bottle or the wet-only methods should be used. In the field validation the results from these two types of collectors were found to be not significantly different within the data quality objectives given by the 4th Daughter Directive [2].

At sites where sedimentation of dry particles is important (e.g. industrial sites) either Bergerhoff collectors or bulk collectors (bottle+funnel method) should be used.

For bottle+funnel methods the precipitation amount shall be measured by weight and no corrections should be made for sampling errors, such as undercatch, evaporation or part of the sample remaining in the collector.

NOTE 1 In southern Europe or other dry climatic regions the dry deposition can be of more importance than was tested in the field validation trial. Under these conditions, the wet-only and the bulk collector (bulk bottle method) can give misleading results. When establishing a new sampling site tests should be made before deciding on the sampling procedure. For bulk collector the deposition on the funnel walls should be analyzed (6.4) to estimate the contribution of deposition on the funnel. In addition, one should carry out filtration tests (7.2.2) to estimate the importance of non-dissolved metals in precipitation samples.

NOTE 2 At high deposition levels both GF-AAS and ICP-MS may be used (see Table 2 to Table 4). For low concentration samples that often can be below the instrumental detection limit of GF-AAS, only ICP-MS is proven to work well.

NOTE 3 At sites with much rainwater and/or snowfall the Bergerhoff collector may be inappropriate due to overflow of the sample collector. For sites with much snow and low temperature the addition of antifreezing and heavy metal free chemicals (e.g. ethylen glycol) can minimize overflow and/or prevent blasting of the collectors.

6.2 Sampling location

The siting requirements should follow the guidelines in Annex III of the 4th Daughter Directive [2], which for deposition measurements in rural areas are harmonized with the guidelines from EMEP [4] and WMO/GAW [5].

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.

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

a) Rural sites: There should 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 [4] for details;

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

6.3 Sampling requirements

Sample devices, measuring equipment, etc. should always be handled with care to prevent contamination. Clean disposable plastic gloves should be used when collecting the samples. The inside of the funnel or the tip of the collector should not be touched. Equipment in the field should always be kept in as clean and dust-free place as possible. It should be particularly avoided to let the equipment be in contact with or close to metal surfaces. The bottles, buckets and funnels should be kept in double sealable plastic bags during transport and storage.

Extra precautions are needed when sampling heavy metals due to the sensitivity for contamination. The concentrations of heavy metals in precipitation are typically only a few nanograms per millilitre and it is important that the SOP is followed carefully.

Immediately after disconnection of the sample bottle or bucket, close it with a screw cap. In order to prevent contamination, the precipitation bottle or bucket should be sent to the laboratory without transferring any precipitation into smaller transport bottles. It is important to avoid leaking during transport.

NOTE 1 In some special cases it can be advisable to transport the collector in a cooling device to avoid algae growth. Acidification of the sample prevents algae growth, but this is usually not done before arrival at the laboratory (7.2.1). Further additives to prevent algae growth or freezing should in general be avoided due to the danger of contamination.

The sample amount in the bulk and wet-only collectors shall be measured by weight. The sample mass is needed to calculate the sample volume (9.1). The precipitation shall be conserved in nitric acid, which is added either before or after the sampling (7.2.1).

NOTE 2 If other measurements like nitrate are carried out at the site, it is recommended to avoid acidification of the sampler before sampling to prevent contamination of these measurements.

Field blanks (3.1.10) shall be taken regularly, e.g. four times a year. These shall be used to check the procedure and not to correct the data. If the field blank is high, i.e. more than 20 % of the average deposition level of the corresponding site, necessary steps shall be taken to find the contamination sources and correct the procedure accordingly.

Examples on how the SOP can be defined for the different collectors are described in Annex A.

6.4 Adsorption and deposition on the funnel walls (bottle+funnel method)

At the start of a sampling program using wet-only or bulk collectors the funnel walls should be rinsed and the rinsing solution analysed to evaluate the importance of adsorption and deposition of As, Cd, Ni, and Pb on the funnel wall. If it turns out to have a significant influence, meaning more than 20 % of the measured deposition, the funnel rinsing needs to be included in the regular sampling procedure.

The funnel should be washed with a known volume (e.g. 200 ml) of diluted nitric acid (e.g. 1 % HNO_3 (5.1.4)), which is collected in a separate collection bottle and sent to the laboratory for analysis, 9.2.

The funnel should regularly be sent to the laboratory for thorough cleaning with nitric acid (5.1.3). The time interval depends on the pollution level.

NOTE 1 During the field test the funnel was cleaned in the laboratory every month.

NOTE 2 If the deposition on the funnel is added to the bulk deposition, the sum is comparable to deposition measured by the Bergerhoff collector.

NOTE 3 The validation programme showed that this rinsing was efficient and more than 90 % of the deposition on the funnel was rinsed off after only one washing procedure.

7 Sample preparation

7.1 Sample storage

The samples shall be stored in a dark and cool environment.

7.2 Preparation of bulk and wet-only samples

7.2.1 Acidification

The samples should be acidified on arrival at the laboratory by adding 1 ml of concentrated nitric acid (5.1.2) per 100 ml sample to dissolve the metals bound to particles or adsorbed to the walls of the container, and to prevent growth of micro-organisms. Acidified samples shall remain in the sampling bottle for at least 24 h.

7.2.2 Filtration of samples from wet-only- and bulk collectors

Even acidified samples, especially those collected at industrial and polluted urban sites, can contain a large fraction of non-dissolved material. Such non-homogenous samples should be filtered before analysis to avoid problems with the analytical instrument. Filtration also ensures that the precipitation sample is homogeneous which make the analysis more reproducible. To filter the acidified samples use either a disposable syringe filter (7.2.2.1) or equipment for vacuum filtration (7.2.2.2).

When new sites are established, it is important that the filters are checked for loss of trace metals with a full digestion of the filters (EN 14902) after vacuum filtration (7.2.2.2). If non-dissolved As, Cd, Ni or Pb make a significant contribution (≥ 20 % of the deposition) of the sample, the whole sample should be vacuum filtered and the filter shall be analysed following the digestion procedure of EN 14902. Alternatively evaporate the whole sample and analyse it in accordance with the Bergerhoff method (7.3).

7.2.2.1 Filtration with disposable syringe filter

Use a disposable syringe filter with a medical single use syringe. A membrane filter (e.g. cellulose acetate; pore size 0,45 µm) shall be used. Filter about 2 ml to 5 ml of the sample to rinse the filter and the syringe and discard the filtrate. Then filter a sufficient amount for analysis into an acid-cleaned bottle. Change the filter and syringe between samples.

Alternatively, in case of small precipitation amount, one may rinse the filter with 1 % HNO_3 (5.1.4).

Prepare filtered blank samples as a control for possible contamination during filtration.

7.2.2.2 Vacuum filtration

Clean all equipment used for filtration thoroughly with 1 % HNO_3 (5.1.4). A membrane filter (e.g. cellulose acetate; pore size 0,45 µm) shall be used.

If sufficient amount of precipitation has been collected, filter about 20 ml to 50 ml of the sample to rinse the filter and discard the filtrate. Then filter 20 ml to 50 ml of the sample into an acid cleaned bottle.

If less than 100 ml precipitation has been collected, filter 20 ml to 50 ml 1 % HNO_3 to rinse the filter and discard the filtrate. Then filter 20 ml to 50 ml of the sample into an acid-cleaned bottle. Change filter and rinse the filtration flask with 1 % HNO_3 between samples.

Prepare filtered blank samples as a control for possible contamination during filtration.

7.3 Preparation of Bergerhoff samples

Pass the content of the Bergerhoff sampling pot through a screen (made of nylon, mesh size: approx. 1 mm) and transfer it completely into an evaporating dish. Remove and transfer any material adhering to the inner gauge walls with the aid of a wiper. Rinse the inner pot, the screen and the wiper with ultrapure water and transfer the rinsing completely into the evaporating dish. Subsequently, evaporate the sample to dryness in a drying device at 105 °C. This process may be repeated with large precipitation amounts.

Carefully add a suitable volume of nitric acid to the dried sample in the evaporating dish. Mix and completely transfer the sample into the digestion vessel using a wiper. Rinse the evaporating dish and the wiper successively with a suitable volume of nitric acid, hydrogen peroxide, and with a suitable volume of ultrapure water (e.g. 8 ml nitric acid (5.1.2), 2 ml hydrogen peroxide (5.1.5) and 2 ml water for a 50 ml digestion vessel size) and transfer the rinsing solution completely into the digestion vessel. The digestion vessel is closed with the associated lid and placed in the microwave digestion system in accordance with the manufacturer's instructions. Alternative digestion mixtures, which have been demonstrated to meet the recovery rate requirements in EN 14902, may also be used.

7.4 Analysis

As far as appropriate, the analytical procedures shall follow the guidelines given in EN 14902. Calculate the instrumental detection limit, see 9.4. The instrumental detection limit should be below 20 % of the expected average concentrations in the samples. In the field trial ICP-MS and GF-AAS were used but only ICP-MS was proven to be satisfactory at low deposition levels, see 10.2.

NOTE As mentioned in the directive 2004/107/EC, other analytical methods may be used if they are proven to give equivalent results for the concentration range in the samples to be analysed.

8 Quality control

The low ambient concentration of heavy metals will easily cause wrong measurements if strict precautions are not taken to prevent contamination and other sources of errors. The laboratories collecting heavy metal data should therefore have a QA procedure, which is designed for their own sampling and analytical procedures. The relevant QA procedure in the laboratory is described in EN 14902.

Labware used for storage of samples shall be properly cleaned before use.

Reagent (3.1.13), laboratory (3.1.11) and field blanks (3.1.10) should be taken regularly to check for potential contamination.

Reagent blanks are part of the normal laboratory QA/QC programme and should be used for calculating the instrumental detection limit (9.4). The laboratory blanks (3.1.11) are used in order to identify potential contamination sources in the laboratory. Reagent and laboratory blanks are usually below the detection limit. For full digestion procedure, the laboratory blanks can be systematically higher. In this case, the results have to be corrected (9.3).

The field blanks shall be used to check if there are problems with the procedures and to calculate the method detection limit (3.1.7). If the field blank is more than 20 % of the average deposition an investigation is necessary, and if possible eliminate any identified sources of contamination. If there is evidence of significant contamination, the result of the associated field samples shall be rejected.

If laboratories carry out analysis of samples of heavy metals in precipitation on a regular basis it is recommended that they participate in a relevant external quality assessment scheme or proficiency testing scheme like participating in laboratory and field intercomparison.

9 Calculation of results

9.1 Calculations of precipitation amount for the wet-only and bulk collectors

The sampling bottle shall be weighed before use and then weighed after the sampling period is finished to determine the mass of the collected sample, see Equation (1). This mass is needed for the determination of the sample volume, see Equation (2).

$$M = M_{tot} - M_c \tag{1}$$

where

M is the sample mass in kilograms (kg);

M_{tot} is the mass of the collector vessel in kilograms (kg) including the sample;

M_c is the mass of the empty sampling collector (bottle or bucket) in kilograms (kg).

For further calculations it is assumed that the sample collected has a density (ρ) of 1 kg/l:

$$V = M / \rho \tag{2}$$

where

V is the sample volume in litres (or cubic decimetres (dm^3));

ρ is the density = 1 kg/l.

9.2 Calculation of deposition in wet-only and bulk collectors

The concentrations of arsenic, cadmium, nickel and lead in precipitation collected in bulk and wet-only should be given in micrograms per litre (µg/l), the deposition in micrograms per square metre day (µg/(m^2 day)). The deposition in the wet-only and bulk collectors shall be calculated following Equation (3):

$$D_a = \frac{C_a \times V}{\pi \times r^2 \times t} \tag{3}$$

where

D_a is the deposition of element *a* in micrograms per square metre day (µg/(m^2 day));

C_a is the concentration of element *a* in micrograms per litre (µg/l);

V is the sample volume in litres (l) or cubic decimetres (dm³);

r is the radius of collector surface in metres (m);

t is the number of days the sampling period lasted.

The amount of arsenic, cadmium, nickel and lead deposited on the funnel wall should similarly be calculated from the concentration in the rinsing solution and precipitation volume using the same equations as above.

For bottle+funnel measurements it is necessary to calculate the deposition on the funnel wall. The deposition on the funnel is given by Equation (4):

$$D_{a(F)} = \frac{C_{a(F)} \times V_F}{\pi \times r^2 \times t} \tag{4}$$

where

$D_{a(F)}$ is the deposition of element *a* on the funnel in micrograms per square metre day (µg/(m^2 day));

$C_{a(F)}$ is the concentration of element *a* in the funnel rinsing solution in micrograms per litre (µg/l);

V_F is the volume of the funnel rinsing solution in litres (l) or cubic decimetres (dm³).

The bottle+funnel deposition is then seen in Equation (5):

$$D_{a(T)} = D_a + D_{a(F)} \tag{5}$$

where

$D_{a(T)}$ is the combined deposition of element *a* in bottle+funnel in micrograms per square metre day (µg/(m^2 day)).

9.3 Calculation of deposition in Bergerhoff collectors

The deposition of arsenic, cadmium, nickel and lead shall be calculated using the mass of the analyte, the surface area of the collector and the sampling time, see Equation (6):

$$D_a = \frac{B_a - B_{b(a)}}{A \times t} \tag{6}$$

where

D_a is the deposition of element *a* in micrograms per square metre day (µg/(m^2 day));

B_a is the mass of element *a* in micrograms (µg);

$B_{b(a)}$ is the mass of laboratory blanks of element *a* in micrograms (µg), see Clause 8;

A is the collecting area in square metres (m^2);

t is the number of days the sampling period lasted.

9.4 Calculation of detection limits

The instrumental detection limit shall be calculated from a minimum of seven replicate analyses of a reagent blank; similarly the method detection limit (3.1.7) shall be calculated from the analysis of a minimum of seven individual field blanks. The instrumental detection limit shall be calculated as micrograms per litre (µg/l) while the method detection limit shall be calculated as micrograms per square metre day (µg/(m^2 day)), see Equation (7):

$$DL_a = t_{(1-0,05)} \times SD_a \qquad with \qquad SD_a = \sqrt{\frac{\sum_{i=1}^{n}(C_{a(i)} - \overline{C_a})^2}{n-1}} \tag{7}$$

where

DL_a is the detection limit of element *a* in micrograms per square metre day (µg/(m^2 day)) or micrograms per litre (µg/l);

SD_a is the standard deviation for element *a* in micrograms per square metre day (µg/(m^2 day)) or micrograms per litre (µg/l);

$t_{(1-0,05)} = t_{95\,\%}$ is the student factor for P = 0,95 (one-sided distribution);

$C_{a(i)}$ is the single value i of the reagent blank of the analyte *a* in micrograms per square metre day (µg/(m^2 day)) or micrograms per litre (µg/l);

$\overline{C}_a$ is the mean value of the blank of the analyte *a* in micrograms per square metre day (µg/(m^2 day)) or micrograms per litre (µg/l);

n is the number of blanks, n ≥ 7.

9.5 Estimation of the measurement uncertainty of the method and performance criteria

In the field trial [3] it was experienced that the sampling uncertainty contributed most to the total uncertainty of the method; in addition, a significant contribution to the overall expanded uncertainty is the choice of collector (see 10.6 and Annex C). It is not expected that laboratories can perform an extensive field trial; however, some important uncertainty assessment should be done by all laboratories. That includes estimate of uncertainty of sampling and analytical procedure. In addition, one should add an additional uncertainty accounting for other contribution uncertainties experienced in the field trial.

To be able to meet the uncertainty criteria given in the 4th Daughter Directive [2] the laboratories should meet the following performance criteria:

a) Relative standard uncertainty of sampling should be below 25 %. This should be assessed by using duplicate or triplicate parallel sampling (i.e. 10.4). This internal standard uncertainty of the method should be calculated using the guidelines from EN ISO 20988 and the equation given in Annex B (see B.7 and B.9);

b) Relative standard uncertainty of analysis should be below 10 %. This should be calculated from laboratory inter-calibration test and using CRM. The standard uncertainty should be calculated using the guidelines from EN ISO 20988 and equation given in Annex B (see B.7 and B.9);

c) An additional relative standard uncertainty component of 20 % should be added to account for possible systematic bias, determined in the field trials described in Annex C, not covered by the two above points: funnel rinsing efficiency, non dissolved metals, choice of collector, and precipitation amount. The individual laboratories may otherwise calculate these contributing uncertainties by doing their own tests.

NOTE These performance criteria are only valid for deposition range given in Table 1.

10 Performance characteristics determined in lab and field tests

10.1 General

The performance characteristics given in this clause are based upon the data gathered in the tests carried out to validate this method [3]. The tests included both laboratory performance and field tests. Five laboratories participated and the field validation tests were carried out at four measurement sites (one industrial, one urban, one remote southern and one remote northern site). The tests included sampling, sample preparation and analysis of the samples. The results from these tests are used to estimate the measurement uncertainty of the methods.

10.2 Method detection limit

The ranges of detection limits obtained by the participating laboratories are given in Table 2. It is differentiated between the two analytical methods because the GF-AAS has generally much higher detection limit than the ICP-MS. A range is not given for the GF-AAS as only one laboratory used this technique.

Table 2 — Detection limits as concentration in bulk and wet only samples

	ICP-MS µg/l		GF-AAS µg/l
	From	To	
As	0,003	0,008	1,20
Cd	0,000 3	0,001	0,01
Ni	0,003	0,02	0,09
Pb	0,002	0,03	0,20

During the field trials the detection limit was estimated using the values in Table 2 multiplied with the minimum detectible precipitation amount (1 mm (5.2.2)) and divided by the number of sampling days (seven days) to get µg/(m^2 day), see Table 3.

Table 3 —Detection limits as deposition for bulk and wet only sampling

	ICP-MS µg/(m^2 day)		GF-AAS µg/(m^2 day)
	From	To	
As	0,000 4	0,001 1	0,17
Cd	0,000 04	0,000 14	0,001 4
Ni	0,000 4	0,002 9	0,013
Pb	0,000 3	0,004 3	0,029

The detection limit for solid samples analysed from blanks using a full digestion procedure is found in Table 4.

Table 4 —Detection limits in solid samples

	ICP-MS µg		GF-AAS µg
	From	To	
As	0,000 8	0,003	0,71
Cd	0,000 1	0,001	0,03
Ni	0,01	1,1	0,57
Pb	0,003	0,02	0,49

During the field trials the detection limit was estimated using the values in Table 4 divided by the area of the collectors (average of 11,7 cm in diameter) and the number of sampling days (28 days) to get µg/(m^2 day), see Table 5.

Table 5 —Detection limits of Bergerhoff samples

	ICP-MS µg/(m^2 day)		GF-AAS µg/(m^2 day)
	From	To	
As	0,003	0,010	2,34
Cd	0,000 3	0,003 3	0,10
Ni	0,33	3,62	1,88
Pb	0,010	0,066	1,61

10.3 Standard uncertainty between laboratories

The standard laboratory uncertainty was calculated using Equation (B.9) in Annex B, B.2, using split samples from the bulk bottle, Bergerhoff and wet-only samples, and the different uncertainties for the collectors are given in Table 6.

Table 6 — Between laboratory relative standard uncertainty

	Bergerhoff	Bulk	Wet-only
As	21 %	12 %	9 %
Cd	26 %	11 %	16 %
Ni	16 %	20 %	24 %
Pb	20 %	14 %	11 %

10.4 Internal standard uncertainty of the different methods

To estimate the relative standard uncertainty for each method, the models A6 and A8 in EN ISO 20988:2007 were used. These equations are given in (B.8) and (B.9) in Annex B, B.2. To calculate this, parallel bulk bottle method (two parallels); bulk bottle+funnel (two parallels); Bergerhoff method (three parallels); and wet-only method (two parallels), combined from all sites, were used. The results are given in Table 7.

Table 7 — Relative standard uncertainty of each method

	Wet-only method	Bulk bottle method	Bulk bottle+funnel method	Bergerhoff method
As	12 %	15 %	6 %	18 %
Cd	13 %	20 %	3 %	5 %
Ni	15 %	24 %	10 %	12 %
Pb	15 %	21 %	8 %	18 %

10.5 Uncertainty calculated using the equation for reproducibility

Two types of similar deposition methods were compared by using the equation for calculating the reproducibility from ISO 5725-2 see B.1. This assessment was done comparing different methods when these are able to be compared. The results obtained with wet-only and bulk bottle methods are similar for rural sites with relatively wet conditions. The results obtained with Bergerhoff and bulk bottle+funnel methods are similar for industrial sites. The results are presented in Table 8.

Table 8 —Uncertainty calculated using the equation for reproducibility

	Wet-only vs. bulk bottle method	Bergerhoff vs. bulk bottle+funnel method
As	16 %	13 %
Cd	17 %	15 %
Ni	26 %	33 %
Pb	17 %	19 %

10.6 Expanded method uncertainty

Following the recommendation from EN ISO 20988, the standard uncertainties of the method in this standard are estimated using parallel independent measurements. The experimental design and valuation method A8 from EN ISO 20988:2007, which is used for parallel application of identical measuring systems under field condition, is appropriate for the field trial measurements. The assessment of uncertainty was done comparing different methods when these are able to be compared. The results obtained with wet-only and bulk bottle methods are similar for rural sites with relatively wet conditions. The results obtained with Bergerhoff and bulk bottle+funnel methods are similar for industrial sites. The expanded uncertainty is calculated using the equation given in B.2 and B.3, and the results are summarised in Table 9.

Table 9 —Expanded uncertainties of the different methods

	Rural (wet condition)	Industrial
	Wet-only vs. bulk bottle method	Bergerhoff vs. bulk bottle+funnel method
As	36 %	42 %
Cd	40 %	51 %
Ni	68 %	(24 %) [a)]
Pb	46 %	64 %

a) Calculated from in between sampler uncertainty for Bergerhoff only because there are no results for the bottle+funnel method with complete digestion.

The field trial demonstrated that the standard method meets the data quality objective of the 4th Daughter Directive [2] expressed as an expanded uncertainty of 70 %.

NOTE For the urban areas, the uncertainty may be similar to rural sites or to industrial depending on the deposition level and the method applied, see 6.1. It was not possible to assess the uncertainty in very dry conditions since none of the sites were representative for this.

11 Reporting of results

The report shall include the following information:

a) Reference to this European Standard and supplementary standards;

b) Identification of the sampling location;

c) Description of location as rural/remote, industrial or urban site;

d) Description of the sampling methods used;

e) Short description of analysis procedure including analytical technique and digestion procedure;

f) Sampling frequency and period;

g) Any unusual features noted during the determination;

h) Results expressed as micrograms per square metre day (μg/(m^2 day));

i) Method detection limit;

j) Expanded uncertainty and how it was estimated.

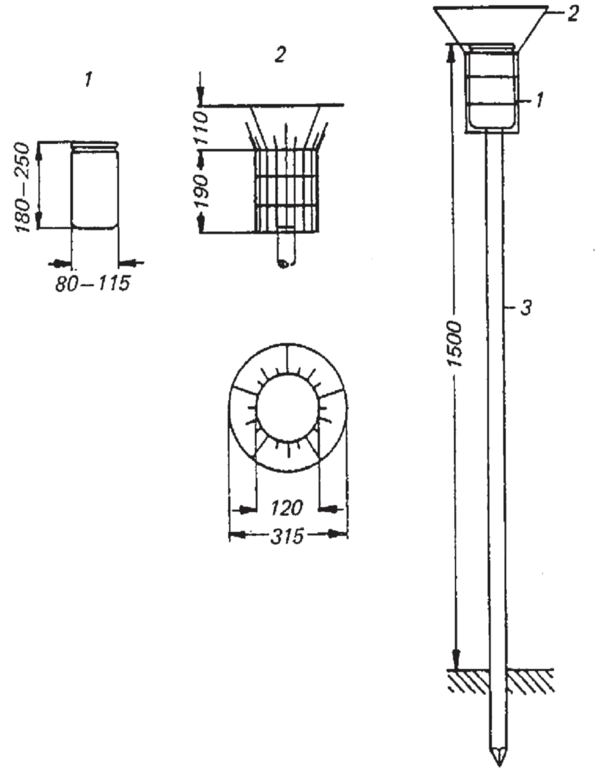
Annex A
(informative)

Standard operating procedures for sampling

A.1 General

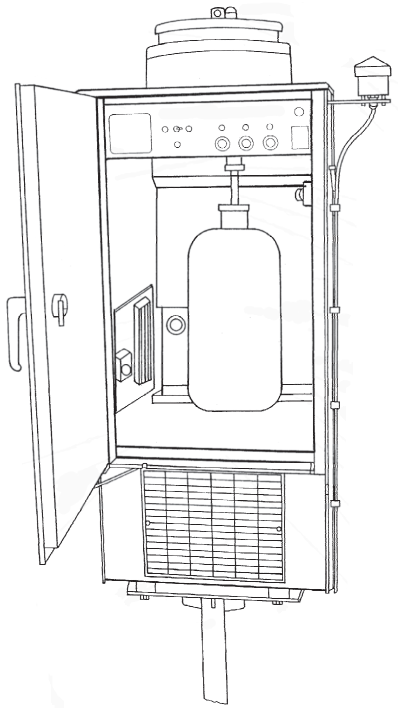
The different types of samplers described in this standard are illustrated in Figures A.1, A.2 and A.3.

Dimensions in millimetres



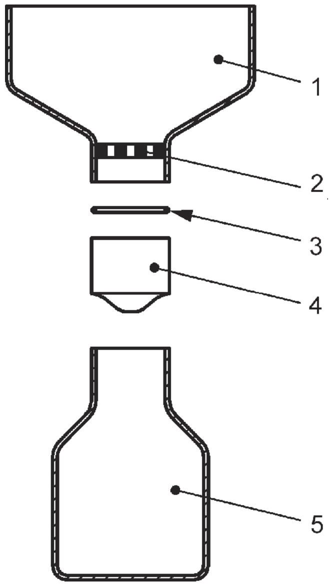
Key
1 collective gauge
2 protective basket
3 post

Figure A.1 — Schematic of a Bergerhoff collector



Dimensions
Height of collection area: ± 1 600 mm
Diameter of funnel: 240 mm
Size of collection bottle: ± 2 l to 5 l

Figure A.2 — Schematic of wet-only collector



Key

1	bulk
2	bug sieve
3	O-ring
4	adapter
5	bottle

Figure A.3 — Schematic of a bulk sampler

Depending on sampling equipment used, follow procedure A.2 or A.3.

A.2 Standard operating procedure for wet-only and bulk sampler

The precipitation shall be conserved in nitric acid which is added either before or just after the sampling.

Some heavy metals can adsorb on the surface of the funnel. The funnel should be washed with a known volume (e.g. 200 ml) of dilute acid (e.g. 1 % HNO_3), which is collected in a separate collection bottle. This shall be analyzed as part of the sample to study the influence of adsorption. This is especially important in the beginning of the sampling program, and if it turns out to have a significant influence at a particular site this needs to be included in the sampling procedure. An example on how the SOP should be is as followed:

a) bring an empty clean precipitation bottle and screw cap to the precipitation sampler;

b) disposable polyethylene gloves are put on. One should change to new gloves if touching the inside of the funnel is necessary;

c) disconnect the precipitation bottle and put on the screw cap;

d) examine the collector funnel for visible contamination such as insects, leaves or tree-needles, organic debris. If this is found, remove the contamination;

e) wash the funnel using 200 ml acidic (1 % HNO_3) water. Let it run into a separate bottle. Disconnect this bottle and set the screw cap on;

f) the frequency for washing the funnel is site dependent. For industrial and urban sites the funnels shall be rinsed weekly, and four weekly rinsing solutions are then combined and analyzed. At the remote sites the funnel should be rinsed before change of the funnel which is done monthly. The 200 ml rinsing solution should be sent to the laboratory;

g) without any collection bottle in place rinse the funnel twice using deionized water (≈ 100 ml) and let the water drain off;

h) connect the new clean precipitation bottle;

i) the precipitation bottle (as well as the bottle with the acidic rinsing water) should be put in separate double plastic bags and sent to the laboratory for analysis;

j) also for periods without rain the empty bottles shall be sent for cleaning;

k) the sampling bottle with screw cap is weighed to determine the precipitation amount;

l) the funnel should regularly be sent to the laboratory for cleaning, the recommended frequency is every month. In the laboratory, the funnel is cleaned with 2 % HNO_3.

The sampling procedures described above are similar for both wet-only and bulk collectors. However, when using bulk collector for snow sampling, the funnel can often be full before the end of the sampling period. The station observer shall therefore take the collector (both funnel and precipitation bottle) indoor whenever it is full, and close the funnel with a polyethylene lid. The lid shall have been cleaned before use and it should be kept on during the entire melting process. While this sample is melting another collector and funnel is installed, and when the sampling period is finished, all samples are sent separately to the laboratory. After acidifying each sample in its sampling bottle, all samples of one sampling period can be poured together in the last collector. Before pouring, the sample should be shaken to include possible solid residue. A major drawback of the bulk sampling approach is the likely reason for contamination due to insects, bird droppings or other material in the sampling vessels. This is especially a problem for extended sampling periods. The risks of contamination are kept under control by using two or three parallel samplers. Contaminated samples can then be identified and discarded.

A.3 Standard operating procedure for the Bergerhoff sampler

The standard operation procedure is based upon the VDI guideline [6].

a) Bring an empty clean bucket, closed with a lid, to the sampling site;

b) Disposable polyethylene gloves are put on;

c) Dismount the exposed bucket from the post and close it tightly with a clean lid wrap it double sealed plastic bags and send it to the laboratory for analysis;

d) Open the empty deposition bottle and mount it into the post.

NOTE It is not necessary to measure the collected water volume, due to evaporative losses during sampling.

Annex B
(informative)

Estimation of the measurement uncertainty of the method

B.1 Calculating the reproducibility

Reproducibility as defined in ISO 5725-2 has been used for calculating reproducibility comparing two types of deposition measurements, i.e. bulk bottle method vs. wet-only and Bergerhoff vs. bulk bottle+funnel.

$$s_{Rj} = \sqrt{s_{rj}^2 + s_{Lj}^2} \tag{B.1}$$

where

$$\mathrm{s}_{\mathrm{rj}}^2 = \frac{\sum_{\mathrm{i=1}}^{\mathrm{n}} (\mathrm{n}_{\mathrm{ij}} - 1)\mathrm{s}_{\mathrm{ij}}^2}{\sum_{i=1}^{n} (n_{ij} - 1)} \quad \textit{and} \quad s_{Lj}^2 = \frac{s_{dj}^2 - s_{rj}^2}{\bar{\bar{n}}_j} \quad \textit{where} \quad s_{dj}^2 = \frac{1}{p-1} \sum_{i=1}^{p} n_{ij} \left(\overline{y_{ij}} - \bar{\bar{y}}_j \right)^2 \tag{B.2}$$

where

s_{Rj}	is the standard deviation of reproducibility;
s_{rj}^2	is the internal standard deviation between each pair of identical samplers (repeatability variance);
s_{Lj}^2	is the inter laboratory standard deviation between each pair of samplers and the overall average (between laboratory variance).

These equations can be simplified when comparing two sets of samplers. When comparing two wet-only samplers (wo) with two bulk bottle samplers this is simplified to:

$$s_{rj}^2 = \frac{1}{2 \times \mathrm{N}} \times \frac{\sum_{i=1}^{n} \left(bulk_{i1} - bulk_{i2}\right)^2 + \left(wo_{i1} - wo_{i2}\right)^2}{4} \tag{B.3}$$

where

N	is the number of samples (weeks);
$bulk_{(i,1or2)}$	is the value determined by the two different bulk samplers for sample *i*;
$wo_{(i,1or2)}$	is the value determined by the two different wet-only samplers for sample *i*.

$$s_{Lj}^{2} = \frac{1}{2\mathrm{N}}\sum_{i=1}^{n}\left(\left(\overline{bulk}_{i} - \overline{y}_{i}\right)^{2} + \left(\overline{wo}_{i} - \overline{y}_{i}\right)^{2} - \frac{s_{rj_{i}}^{2}}{2}\right) \tag{B.4}$$

where

$\overline{bulk_i}$	is the average between the values determined by the two bulk samplers for sample *i*;
$\overline{wo_i}$	is the average between the values determined by the two wet-only samplers for sample *i*;
$\overline{y}_i$	is the average between the values determined by the wet-only and bulk sampler for sample *i*.

When comparing Bergerhoff (BH) and bulk bottle+funnel method (BF) it will similarly be:

$$s_{rj}^{2} = \frac{1}{2\mathrm{N}} \times \frac{\sum_{i=1}^{n}\left(BH_{i1} - \overline{BH}_{i}\right)^{2} + \left(BH_{i1} - \overline{BH}_{i}\right)^{2} + \left(BH_{i1} - \overline{BH}_{i}\right)^{2} + 2\times\left(BF_{i1} - BF_{i2}\right)^{2}}{5 \quad (= no \quad of \quad samplers)} \tag{B.5}$$

$$s_{Lj}^{2} = \frac{1}{2\mathrm{N}}\sum_{i=1}^{n}\left(\left(\overline{BH}_{i} - \overline{y}_{i}\right)^{2} + \left(\overline{BF} - \overline{y}_{i}\right)^{2} - \frac{s_{rj_{i}}^{2}}{2}\right) \tag{B.6}$$

where

$\overline{BH_i}$	is the average between the values determined with the three Bergerhoff samplers for sample *i*;
$BF_{(i,1 or 2)}$	is the value determined with the two different bulk and funnel samplers for sample *i*;
$\overline{BF_i}$	is the average between the values determined with the two bulk and funnel samplers for sample *i*;
$\overline{y}_i$	is the average between the values determined with the Bergerhoff and bulk and funnel samplers for sample *i*.

B.2 Calculating the sampler uncertainty

Following the recommendation from EN ISO 20988, the standard uncertainty is estimated using parallel independent measurements. The experimental design and valuation method A8 from EN ISO 20988:2007, which is used for parallel application of identical measuring systems under field condition, is appropriate for the field trial measurements. This is a direct approach, type A, including variations and uncorrected biases.

$$u(y) = \sqrt{\frac{\sum_{j=1}^{N} s_{(j)}{}^{2}}{N}} \tag{B.7}$$

where

$u(y)$ is the standard uncertainty;

N is the number of samples;

$s_{(j)}$ is the standard deviation in each trial *j*:

$$s_{(j)} = \sqrt{\frac{\sum_{k=1}^{K}(y_{k,j} - y_{R(j)})^2}{(K-1)}} \quad where \quad y_{R(j)} = \frac{\sum_{k=1}^{K} y_{(k,j)}}{K} \text{ and} \qquad \text{(B.8)}$$

$y_{(k,j)}$ is the observed value in parallel *k*, trial *j;*

K is number of parallels in trial *j.*

For K = 2 the formula defined in (B.7) is identical to what is defined in A6 in EN ISO 20988:2007:

$$u(y) = \sqrt{\frac{\sum_{J=1}^{N} (y_{(1,j)} - y_{(2,j)})^2}{2N}} \qquad \text{(B.9)}$$

where

$u(y)$ is the standard uncertainty;

$y_{(1,j)}$ is the observed value in parallel 1;

$y_{(2,j)}$ is the observed value in parallel 2;

N is the number of samples.

The relative standard uncertainty is calculated dividing the average concentration from the datasets with the standard uncertainty.

These uncertainties are used for calculating the between sampler uncertainties, the between laboratory uncertainties and when comparing the different methods, i.e. bulk bottle method vs. wet-only and Bergerhoff vs. bulk bottle+funnel.

B.3 Calculating the expanded uncertainty

The calculations in B.2 are used for evaluating the uncertainty of the measurements. The relative expanded uncertainty U is then calculated by using a coverage factor k, corresponding to a level of confidence of approximately 95 %. The coverage factor (k) of 2 is used if there are more than 20 parallel samples; otherwise the *Student t-factor* is used:

$$U_p(y) = k \times u(y) \qquad \text{(B.10)}$$

where

$U_p(y)$ is the expanded uncertainty*;*

$u(y)$ is the standard uncertainty;

k is the coverage factor.

Annex C
(informative)

Uncertainty budget

The field validation test covered parallel and split sampling at four different types of sites with three types of collectors. From these different tests it is possible to assess the different contributions to the overall uncertainty using a so-called indirect approach. This type B evaluation is a supplement to the type A evaluation given in 10.6.

In Table C.1 the different contributions for the uncertainty are listed which have been assessed during the field and lab trials. The example is given for Cd, but similar can be done for the different elements. There are some variations between the elements, especially Ni that has a higher uncertainty due to possible inhomogeneity.

Table C.1 — List of all considered standard uncertainty contributions for cadmium (Cd)

Contribution	**Covered by**	**Wet-only**	**Bulk**	**Bulk+ funnel**	**Bergerhoff**
Analytical	Laboratory inter-comparison (lab trial)	3 %	3 %	3 %	3 %
Sampling	Internal standard uncertainty of the method (Table 7)	13 %	20 %	3 %	5 %
Sample preparation	Split samples. This includes both analytical uncertainty and transport and sample preparation (Table 6)	16 %	11 %	11 %	26 %
Non dissolved metal	From filter test	Not applicable	Not applicable	Not applicable	Not applicable
Precipitation amount	From external inter-comparison and comparison at the field trials	7 %	5 %	5 %	Not applicable
Efficiency of funnel rinsing	From funnel rinsing test	Not applicable	Not applicable	10 %	Not applicable
Unaccounted dry deposition during dry periods	Test of particulate deposit in collector after periods with no rain	Not applicable	<0,5 %	<0,5 %	Not applicable
Choice of collector	Difference between total uncertainty (Table 9 non expanded) and uncertainty of the method (Table 7)	7 %	1 %	18 %	16 %
Combined standard uncertainty	Square root of the sum of square of the contribution uncertainties. Not including the analytical since that is part of sample preparation.	23 %	23 %	22 %	31 %
Expanded uncertainty	Using a coverage factor of 2	46 %	47 %	44 %	62 %

Annex ZA
(informative)

Relationship between this European Standard and the essential requirements of EU Directives

This European Standard has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association and supports essential requirements of the European Council Directive on Ambient Air Quality Assessment and Management [1] and the 4th Daughter Directive [2].

WARNING — Other requirements and other EU Directives may be applicable to the product(s) falling within the scope of this standard.

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