

# SLOVENSKI STANDARD

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

Luftbeschaffenheit - Messverfahren zur Bestimmung von Arsen, Cadmium, Blei und Nickel in atmosphärischer Deposition

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

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EUROPEAN STANDARD  
NORME EUROPÉENNE  
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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 dépôts d'arsenic, de cadmium, de nickel  
et de plomb

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

This European Standard was approved by CEN on 17 October 2009.

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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of an identical text or by endorsement, at the latest by May 2010, and conflicting national standards shall be withdrawn at the latest by May 2010.

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.

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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 4<sup>th</sup> 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 ( $\mu\text{g}/\text{m}^2 \text{ day}$ )	Upper limit ( $\mu\text{g}/\text{m}^2 \text{ day}$ )
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 PM<sub>10</sub> 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.

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## 3.1.9

**expanded uncertainty****expanded measurement uncertainty**

quantity defining an interval  $[y - U_p(y); y + U_p(y)]$  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

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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<sub>3</sub>), 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<sub>2</sub>O<sub>2</sub>), 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.

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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.