SLOVENSKI STANDARD
SIST EN 14902:2005

01-december-2005

Kakovost zunanjega zraka – Standardna metoda za določevanje Pb, Cd, As in Ni v frakciji PM10 lebdečih delcev

Ambient air quality - Standard method for the measurement of Pb, Cd, As and Ni in the PM10 fraction of suspended particulate matter

Außenluftbeschaffenheit - Standardisiertes Verfahren zur Bestimmung von Pb/Cd/As/Ni als Bestandteil der PM10-Fraktion des Schwebstaubes

iTeh STANDARD PREVIEW
(standards.iteh.ai)

Qualité de l'air ambiant - Méthode normalisée de mesure du plomb, du cadmium, de l'arsenic et du nickel dans la fraction MP10 de matiere particulaire en suspension

Ta slovenski standard je istoveten z: **EN 14902:2005**

ICS:

13.040.20   Kakovost okoljskega zraka   Ambient atmospheres

SIST EN 14902:2005   **en,fr,de**

iTeh STANDARD PREVIEW
(standards.iteh.ai)

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 14902

August 2005

ICS 13.040.20

English version

Ambient air quality - Standard method for the measurement of Pb, Cd, As and Ni in the PM10 fraction of suspended particulate matter

Qualité de l'air ambiant - Méthode normalisée pour la mesure de Pb, Cd, As et Ni dans la fraction MP10 de la matière particulaire en suspension

Außenluftbeschaffenheit - Standardisiertes Verfahren zur Bestimmung von Pb/Cd/As/Ni als Bestandteil der PM10 Fraktion des Schwebstaubes

This European Standard was approved by CEN on 27 June 2005.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: rue de Stassart, 36   B-1050 Brussels

Ref. No. EN 14902:2005: E

EN 14902:2005 (E)

Contents

2

Foreword

This European Standard (EN 14902:2005) 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 February 2006, and conflicting national standards shall be withdrawn at the latest by February 2006.

This European Standard has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association (see Annex ZA).

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

EN 14902:2005 (E)

1   Scope

This European Standard specifies a method for the determination of particulate lead (Pb), cadmium (Cd), arsenic (As) and nickel (Ni) in ambient air that can be used in the framework of the European Council Directive on Ambient Air Quality Assessment and Management [1] and the 1st [2] and 4th [3] Daughter Directives. Performance requirements with which the method has to comply are specified in this European Standard. The performance characteristics of the method were determined in comparative field validation tests carried out at four European locations (see [4]).

This European Standard specifies a method for sampling of Pb, Cd, As and Ni as part of the PM10 aerosol, microwave digestion of the samples and analysis by graphite furnace atomic absorption spectrometry or by inductively coupled plasma (quadrupole) mass spectrometry.

This European Standard is applicable for the measurement of Pb, Cd, As and Ni as part of the PM10 aerosol fraction in the concentration ranges listed in Table 1.

Table 1 — Working ranges of the method in ng/m³

	From	To
Pb	1	4 000
Cd	0,1	50
As	0,5	350
Ni	2	100

The actual lower limits of the working ranges depend upon the variability of the laboratory filter blank (5.3.1). The lower limits of the working ranges given in Table 1 are expected values based upon performance achieved in the field validation tests. Similarly the upper limits of the working ranges have been set arbitrarily based upon the maximum daily values measured during the field validation tests. The method can be applied to higher concentrations provided the PM10 collection characteristics of the sampler are not compromised.

2   Normative references

The following referenced documents are indispensable for the application of this European Standard. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 12341:1998, *Air quality – Determination of the PM10 fraction of suspended particulate matter – Reference method and field test procedure to demonstrate reference equivalence of measurement methods.*

ENV 13005:1999, *Guide to the expression of uncertainty in measurement[1]*

3   Terms, definitions and abbreviations

3.1 Terms and definitions

For the purpose of this European Standard, 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 metalloid of interest present in the sample

3.1.2
blank solution
solution prepared from a laboratory filter blank or a field filter blank by the process of sample dissolution

NOTE   A laboratory filter blank solution or a field filter blank solution might need to be subjected to further operations, e.g. dilution and/or addition of an internal standard(s), if such operations are applied to the sample solutions in order to produce test solutions that are ready for analysis.

3.1.3
calibration blank solution
calibration solution prepared without addition of stock standard solution or working standard solution, for which the concentration of the analyte(s) of interest is considered to be zero

3.1.4
calibration solution
solution used for calibration of the analytical instrument, containing the analyte(s) of interest at (a) suitable concentration(s), prepared by dilution of the stock standard solution(s) or the working standard solution(s)

NOTE   The technique of matrix-matching is normally used when preparing calibration solutions.

3.1.5
certified reference material
reference material, in which one or more of property values are certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation that is issued by a certifying body [5]

3.1.6
field filter blank
filter that is taken through the same procedure as a sample, except that no air is drawn through it. It is transported to the sampling site, mounted in the sampling unit, dismounted, returned to the laboratory and worked up in the same way as a sample

---

[1] Equal to ISO Guide 30 (GUM) Geneva 1993.

EN 14902:2005 (E)

3.1.7
internal standard solution
solution added to sample, blank and calibration solutions to correct for instrumental fluctuations during analysis, containing (a) suitable element(s) at (a) suitable concentration(s)

3.1.8
instrumental detection limit
lowest amount of an analyte that is detectable using an instrument, as determined by repeated measurements of a reagent blank

3.1.9
laboratory filter blank
unused filter that does not leave the laboratory and is taken through the same analytical procedure as a sample. This filter is taken from the same batch as used for sampling

3.1.10
limit value
level fixed on the basis of scientific knowledge, with the aim of avoiding, preventing or reducing harmful effects on human health and/or the environment as a whole, to be attained within a given period and not to be exceeded once attained

3.1.11
matrix interference
non-spectral interference
matrix effect
interference of a non-spectral nature caused by a difference between the matrix of the calibration and test solutions

3.1.12
matrix-matching
technique, used to minimise the effect of matrix interferences on analytical results, that involves preparation of calibration solutions in which the concentrations of acids and other major solutes are matched with those in the test solutions

3.1.13
method detection limit
lowest amount of an analyte that is detectable using the method, as determined by analysis of laboratory filter blanks

3.1.14
PM10
target specification for sampling the thoracic particles
[EN 12341:1998]

3.1.15
PM10 reference sampler
by convention, a sampling instrument that possesses the required performance characteristics, in order to assess the PM 10 mass concentration
[EN 12341:1998]

3.1.16
PM10 sampler
sampling instrument whose performance has been demonstrated to be equivalent to a PM 10 reference sampler

3.1.17
quality control solution
solution that is analysed together with the sample solutions to provide information on the repeatability of the analytical method, results for which are plotted on a quality control chart to verify that a method is performing satisfactorily

3.1.18
quantification limit
lowest amount of an analyte that is quantifiable with a given confidence level using the method, as determined by analysis of laboratory filter blanks

3.1.19
reagent blank solution
solution that contains all the reagents used during the analysis of the sample, but without the sample and filter matrix

3.1.20
repeatability (of results of measurements)
closeness of the agreement between the results of successive measurements of the same measurand carried out under the same conditions of measurement [6]

3.1.21
reproducibility (of results of measurements)
closeness of the agreement between the results of measurements of the same measurand carried out under changed conditions of measurement [6]

3.1.22
sample solution
solution prepared from a sample by the process of sample dissolution

NOTE   A sample solution might need to be subjected to further operations, e.g. dilution and/or addition of an internal standard(s), in order to produce a test solution that is ready for analysis.

3.1.23
sampling method
all steps of the measuring procedure that describe the process of collecting an air sample

3.1.24
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

3.1.25
sample digestion
sample dissolution
process of obtaining a solution containing the analytes of interest from a sample. This can involve complete dissolution of the sample

3.1.26
stock standard solution
solution used for preparation of calibration solutions, containing one or more of the analyte(s) of interest at (a) concentration(s) traceable to national or International Standards

3.1.27
sub-sample (of a filter)
part of a large filter, cut out for analytical reasons, that is representative of the whole

3.1.28
suspended particulate matter
notion of all particles surrounded by air in a given, undisturbed volume of air
[EN 12341:1998]

3.1.29
target value
concentration in the ambient air fixed with the aim of avoiding, preventing or reducing harmful effects on human health and the environment as a whole, to be attained where possible over a given period [3]

EN 14902:2005 (E)

3.1.30
test solution
blank solution or sample solution that has been subjected to all operations required to bring it into a state in which it is ready for analysis, e.g. dilution and/or addition of an Internal Standard(s)

NOTE   If subject to no further operations before analysis, then the blank test solution is identical to the blank solution. The same is true for the sample test solution and sample solutions.

3.1.31
uncertainty (of a measurement)
parameter associated with the result of a measurement that characterises the dispersion of the values that could reasonably be attributed to the measurand
[ENV 13005:1999]

3.1.32
working standard solution
solution prepared by dilution of the stock standard solution(s), that contains the analyte(s) of interest at (a) concentration(s) better suited to preparation of calibration solutions

3.2 Abbreviations

AAS   atomic absorption spectrometry;

amu   atomic mass unit;

CRM   certified reference material;

GFAAS   graphite furnace atomic absorption spectrometry;

HDPE   high density polyethylene;

HVS   high volume sampler, as described in EN 12341:1998, Annex B.2;

ICP-MS   inductively coupled plasma – mass spectrometry;

LDPE   low density polyethylene;

LVS   low volume sampler, as described in EN 12341:1998, Annex B.1;

PFA   perfluoroalkoxy polymer;

PP   polypropylene;

PTFE   polytetrafluoroethylene;

SPM   suspended particulate matter;

TFM   tetrafluoromethoxil polymer.

4   Principle

The method is divided into two main parts: first the sampling in the field and second the analysis in the laboratory. During sampling, particles containing Pb, Cd, As and Ni are collected by drawing a measured volume of air through a filter mounted in a sampler designed to collect the PM10 fraction of suspended particulate matter. The sample filter is transported to the laboratory and Pb, Cd, As and Ni are taken into solution by closed vessel microwave digestion using nitric acid and hydrogen peroxide. The resultant solution is analysed by GFAAS or ICP-MS.

8

5   Requirements

5.1 Siting requirements

The requirements for siting samplers given in the 1st Daughter Directive [2] (for Pb) and the 4th Daughter Directive [3] (for Cd, As and Ni) shall be followed.

5.2 Sampling requirements

Sampling shall be performed using a PM10 sampler complying with the requirements of EN 12341. In general the sampling time should be 24 h. However, low concentrations could require longer sampling times, whereas high concentrations could require shorter ones.

NOTE   In order to meet the requirements of this European Standard, particularly with respect to detection limits, it might be necessary to increase the sampling time for samplers that have low flow rates.

5.3 Analytical requirements

5.3.1   Method detection limit

The method detection limits, based on laboratory filter blanks, shall be less than or equal to 10 % of the limit value for Pb and less than or equal to 10 % of the target values for Cd, As and Ni, as specified in the 1st and 4th Daughter Directives [2], [3]. The method for calculating method detection limits is described in 11.5.

NOTE   If it is necessary to perform measurements at lower concentrations within the working ranges of the method given in Table 1, lower method detection limits will be necessary (see Table 7).

5.3.2   Recovery rate

The average recovery rates for the method, when determined in accordance with the procedure described in 10.3, shall meet the requirements for recovery rates given in Table 2.

Table 2 — Minimum requirements for average recovery rates

	Range of average recovery rates [%]
Pb	90 to 110
Cd	90 to 110
As	85 to 115
Ni	85 to 115

5.3.3   Homogeneity requirement for sub-samples

The relative standard deviation of the lead content of sub-samples, when determined in accordance with the procedure described in 9.6, shall not exceed 5 %.

EN 14902:2005 (E)

6 Reagents and gases

6.1 Water, ultrapure, distilled or deionised.

NOTE   It is recommended that the water used be obtained from a water purification system that delivers ultrapure water having a resistivity of 0,18 MΩ ·m or greater at 25 °C.

6.2 Nitric acid (HNO₃), concentrated, ρ 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 10 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. Use suitable personal protective equipment (including suitable gloves, face shield or safety spectacles, etc) when working with the concentrated or dilute nitric acid.

6.3 Nitric acid for cleaning purposes, add approximately 800 ml of ultrapure water (6.1) to a 1 litre one-mark volumetric flask. Carefully add 100 ml of concentrated nitric acid (6.2) to the flask and swirl to mix. Allow to cool, dilute to 1 l with water and mix thoroughly.

6.4 Hydrogen peroxide (H₂O₂), mass fraction about 30 %, high purity grade [concentration stated by the manufacturer or supplier < 0,005 mg/l for As, Cd, Ni and Pb (typical concentrations are generally 10 times lower)].

WARNING   Hydrogen peroxide is corrosive and oxidising. Avoid exposure by contact with the skin or eyes. Use suitable personal protective equipment (including suitable gloves, face shield or safety spectacles, etc) when working with hydrogen peroxide.

6.5 Stock standard solutions, single element or multi-element. Use commercial standard solutions with certified concentrations traceable to national or International Standards. Observe the manufacturer's expiration date or recommended shelf life.

6.6 Working standard solution, prepare a working standard solution containing the analyte(s) of interest at a concentration(s) that is better suited to preparation of the calibration solutions, if desired, by appropriate dilution of the stock standard solutions (see 6.5).

6.7 Matrix modifier, e.g. NH₄H₂PO₄, Mg(NO₃)₂ or Pd(NO₃)₂, or a combination of these, if required, for GFAAS analysis.

6.8 Argon, liquid or cylinder of a purity suitable for use in GFAAS or ICP-MS analysis.

6.9 Certified Reference Material (CRM), with a sample matrix that is as representative as possible of ambient air PM10 particulate matter [2]).

---

[2]) "NIST 1648 "Urban Particulate Matter" from *National Institute of Standards & Technology*, USA, 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. NIST 1648 was used as reference material during the validation of the method and is named in the text as CRM 1."

7 Apparatus

7.1 Sampling equipment

7.1.1 **PM10 samplers**, equivalent to EN 12341. HVS or LVS may be used and the samplers may be single-filter devices or sequential samplers.

NOTE   To minimise contamination of the sample, all components of the filter holder in contact with the filter should be made of a suitable material with as low a metal content as possible, such as PTFE, glass, quartz etc.

7.1.2 **Greasing agent**, if required, suitable for greasing the sampler impaction plate.

7.1.3 **Filters**, of a diameter suitable for use with the samplers (7.1.1), with a separation efficiency of at least 99,5 % at an aerodynamic diameter of 0,3 µm. Each new batch of filters shall be tested to confirm that the filter blank variability is sufficiently low so that the method detection requirements of 5.3.1 are met.

NOTE 1   It is recommended that filters used should be sourced from a manufacturer who has determined the separation efficiency of the filter material according to standard methods such as [8] or [9].

NOTE 2   The metal content of the filter should be as low as possible because it is usually the case that higher filter blank values lead to higher variability of the blank values.

NOTE 3   Quartz fibre filters, cellulose nitrate and cellulose acetate membrane filters have been found suitable in the field validation tests (see Annex B). Further information can be found in [10].

NOTE 4   In choosing a filter, the user should consider the initial pressure drop across the filter and the increase in this that occurs due to the collection of the dust and ensure that there is no possibility of an excessive pressure drop developing during sampling. This depends on the type of filter (i.e. membranes), unusual high concentrations of PM10, the use of longer sampling time than 24 h and the capability of the sampling device to handle the resulting pressure drop. Quartz fibre filters are proven to be efficient in most cases although they have weak mechanical properties.

7.1.4 **Flowmeter**, with a measurement uncertainty that is sufficient to enable the volumetric flow rate of the samplers (7.1.1) to be measured to within ± 5 %. The calibration of the flowmeter shall be traceable to (inter)national standards.

NOTE   It is recommended that the flowmeter used should be capable of measuring the volumetric flow rate to within ± 2 % or better.

7.2 Laboratory apparatus

Ordinary laboratory apparatus, and 7.2.1- 7.2.7.

7.2.1 **Microwave digestion system**, designed for closed vessel sample digestion in the laboratory, with power output regulation, fitted with a temperature control system capable of sensing the temperature and automatically adjusting the microwave power output. The microwave cavity shall be corrosion resistant and well ventilated, with all electronics protected against corrosion to ensure safe operation.

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.

WARNING Ensure that the manufacturer's safety recommendations are followed.

7.2.2 **Sample vessels**, designed for high pressure microwave digestion, having a system for controlled pressure relief, capable of withstanding an operating temperature of 220 °C and a pressure of at least 50 bar, and having an internal volume of at least 50 ml, e.g. vessels having an inner liner and cover made of a microwave transparent and chemically resistant material (usually a fluorocarbon polymer such as TFM or PFA).

7.2.3   One-mark volumetric flasks, made of borosilicate glass, quartz, polyethylene or fluorocarbon polymer.

NOTE   Solutions with ultra-trace level analytes are commonly stored in thoroughly cleaned vessels made of polyethylene (LDPE, HDPE) or fluorocarbon polymer (e.g. PFA, PTFE).

7.2.4   Punching tool, if required, suitable for taking sub-samples of large filters without contamination.

7.2.5   Transport containers, suitable for transport of filters from the sampling site back to the laboratory, made of inert low metal background materials such as HDPE, PP, polycarbonate, PTFE, glass or quartz.

Either

7.2.6   Graphite furnace atomic absorption spectrometer, 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 (see 5.1.5 of [11]) or using a Zeeman background correction system.

Or

7.2.7   Inductively coupled plasma - mass spectrometer, quadrupole instrument capable of scanning the mass range from 5 amu to 250 amu with a minimum resolution capability of 1 amu 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.

8   Sampling

8.1 Preparation of the sampling equipment

8.1.1   Consult the manufacturer's instruction manual to determine the minimum voltage and power requirements of the sampler (7.1.1) and ensure that an adequate power supply is available at the sampling site.

8.1.2   Clean the sampler inlet, suction pipe, filter change mechanism, filter cassettes and all other parts of the sampler that can come in contact with the filter before use according to the manufacturer's specifications. Similarly, inspect greased parts like impaction plates before use, clean them if necessary and grease them again.

8.2 Handling of filters

Handle small filters using non-metallic and non-serrated blunt tweezers, so as to avoid contamination and damage. For large filters this procedure might not be practicable, in which case handle them carefully using gloves made of an appropriate material (e.g. non-powdered vinyl gloves), touching only the outside edges of the filters.

8.3 Preparation of filters

8.3.1   Reject filters that could have been contaminated, e.g. during packing and/or transport.

8.3.2   Inspect each filter before use for pin holes and other imperfections, such as chaffing, loose material, discoloration and non-uniformity. For example, use a magnifying lens with a light or check in front of an area light. Reject any filter if its integrity is suspect.

8.3.3 Assign each filter a unique identifier and place it in a labelled, sealed container (7.2.5) for storage and transportation to the field. If the filter has to be marked for identification purposes, do not mark it in an area of the filter that will be analysed.

8.3.4 Establish a filter log (i.e. a chain of custody book/record) in which to document the use of each filter. Record the lot number of the filters used in the filter log. If the sampler to be used is a sequential sampler that operates continuously for a programmed period, load the required number of filters into a labelled filter cartridge and seal it ready for transportation to the field. Record details of which filter was loaded into which position in the cartridge.

8.3.5 Take laboratory filter blanks (see 3.1.9) periodically during preparation of a batch of filters, so that the number of laboratory filter blanks is at least 5 % of the number of filters that will be used for sampling in the field.

8.4 Sample collection

8.4.1 Set up the sampler (7.1.1) in the field according to the manufacturer's instructions, ensuring that the siting requirements in 5.1 are met.

8.4.2 Carry out a leak test and check the flow rate of the sampler using the calibrated flowmeter (7.1.4) before use and at least every three months, following the manufacturer's instructions. If the flow rate deviates by more than 5 % from its nominal value, calibrate the sampler by adjusting the flow rate as necessary.

NOTE   It is recommended that a leak test and a flow rate calibration are carried out in the laboratory in order to identify problems with the sampler at an early stage.

8.4.3 Take field filter blanks (see 3.1.6) periodically at each site (at least once for every 20 filters used for sampling).

8.4.4 Load either an unexposed filter (for single filter devices) or a cartridge of unexposed filters (for sequential samplers) into the sampler at the start of the sampling period. Program the sampler following the manufacturer's instructions, start the timer and record details of the start time, flow rate and filter code(s) in the filter log.

8.4.5 Collect the filter from the sampler at the end of the sampling period, replace it in its uniquely marked transport container and seal it for transportation to the laboratory (for single filter devices). For sequential samplers, collect the cartridge of used filters and prepare it for transportation to the laboratory.

NOTE   If filters are folded for storage (for easier transportation), then it will be necessary to analyse the whole filter as folding can affect the distribution of particles on the filter surface.

8.4.6 Record full details of each sample in the filter log, including the stop time, the flow rate, the air sample volume, in m³; any mechanical or electrical failures, the meteorological conditions during the sampling period and any other data that could be important for later evaluation of the sampling.

8.4.7 Clean and grease the inlet impaction plate, if applicable, at least once every 15 d of sampling. Perform intensive cleaning of the PM10 sampling head according to the manufacturer's instructions at least once every six months.