SLOVENSKI STANDARD
SIST ISO 11174:1997

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Zrak na delovnem mestu - Ugotavljanje kadmijevega prahu in kadmijevih spojin - Plamenska in elektrotermična atomska absorpcijska spektrometrijska metoda

Workplace air -- Determination of particulate cadmium and cadmium compounds -- Flame and electrothermal atomic absorption spectrometric method

Air des lieux de travail -- Dosage du cadmium particulaire et des composés particulaires du cadmium -- Méthode par spectrométrie d'absorption atomique dans la flamme et méthode par spectrométrie d'absorption atomique avec atomisation électrothermique

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Workplace air — Determination of particulate cadmium and cadmium compounds — Flame and electrothermal atomic absorption spectrometric method

Air des lieux de travail — Dosage du cadmium particulaire et des composés particulaires du cadmium — Méthode par spectrométrie d'absorption atomique dans la flamme et méthode par spectrométrie d'absorption atomique avec atomisation électrothermique

Reference number
ISO 11174:1996(E)

Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 11174 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 2, *Workplace atmospheres*.

Annexes A and B of this International Standard are for information only.

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INTERNATIONAL STANDARD © ISO **ISO 11174:1996(E)**

Workplace air — Determination of particulate cadmium and cadmium compounds — Flame and electrothermal atomic absorption spectrometric method

WARNING — Cadmium and cadmium compounds are toxic and are suspected human carcinogens (see reference [1] in annex B). Avoid any exposure by inhalation. Personal protection (e.g. an effective respirator) must be used in all cases where exposure to cadmium or cadmium compounds is possible.

1 Scope

This International Standard specifies a method for the determination of the mass concentration of particulate cadmium and cadmium compounds in workplace air, using either flame or electrothermal atomic absorption spectrometry.

The sample digestion procedure specified in 8.2.2 has been validated (see reference [2] in annex B) for a selection of cadmium compounds and pigments and glass enamels containing cadmium.

The analytical method has been validated (see reference [2] in annex B) for the determination of masses of 10 ng to 600 ng of cadmium per sample using electrothermal atomic absorption spectrometry, and 0,15 µg to 96 µg of cadmium per sample using flame atomic absorption spectrometry. The concentration range for cadmium in air for which this procedure is applicable is determined in part by the sampling procedure selected by the user.

The method is applicable to personal sampling of the inhalable or respirable fraction of airborne particles, as defined in ISO 7708, and to fixed-location sampling.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 648:1977, *Laboratory glassware — One-mark pipettes.*

ISO 1042:1983, *Laboratory glassware — One-mark volumetric flasks.*

ISO 3585:1991, *Borosilicate glass 3.3 — Properties.*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods.*

ISO 6955:1982, *Analytical spectroscopic methods — Flame emission, atomic absorption and atomic fluorescence — Vocabulary.*

ISO 7708:1995, *Air quality — Particle size fraction definitions for health-related sampling.*

ISO 8655-1:—[1], *Piston and/or plunger operated volumetric apparatus (POVA) — Part 1: Definitions.*

ISO 8655-2:—[1], *Piston and/or plunger operated volumetric apparatus (POVA) — Part 2: Operating considerations.*

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[1] To be published.

ISO 8655-3:—[1], *Piston and/or plunger operated volumetric apparatus (POVA) — Part 3: Methods of test.*

ISO 8655-4:—[1], *Piston and/or plunger operated volumetric apparatus (POVA) — Part 4: Specifications.*

ISO 8756:1994, *Air quality — Handling of temperature, pressure and humidity data.*

EN 482:1994, *Workplace atmospheres — General requirements for the performance of procedures for the measurement of chemical agents.*

EN 1232:—[1], *Workplace atmospheres — Pumps for personal sampling of chemical agents — Requirements and test methods.*

3 Principle

3.1 Particulate cadmium and cadmium compounds are collected by drawing a measured volume of air through a filter mounted in a sampler designed to collect either the inhalable fraction of airborne particles or the respirable fraction of airborne particles, as appropriate (see note 17).

3.2 A test solution is prepared by treating the filter and collected sample with 5 ml of nitric acid diluted 1 + 1, heating on a hotplate until about 1 ml of concentrated nitric acid solution remains, allowing the solution to cool and then diluting to 10 ml with water.

3.3 The test solution is analysed for cadmium by aspirating into the oxidizing air/acetylene flame of an atomic absorption spectrometer equipped with a cadmium hollow cathode lamp or electrodeless discharge lamp. Absorbance measurements are made at 228,8 nm and results are obtained by the analytical-curve technique (see ISO 6955:1982, subclause 6.1.1).

3.4 For accurate determination when the concentration of cadmium in the solution is low, the analysis may be repeated using electrothermal atomic absorption spectrometry. Aliquots of the test solution and a matrix-modifier solution are injected onto a solid, pyrolytic graphite platform mounted in a pyrolytically coated graphite tube, and after the drying and sample ashing stages the sample is atomized electrothermally. Absorbance measurements are made at 228,8 nm with background correction and results are obtained by the analytical-curve technique (see ISO 6955:1982, subclause 6.1.1).

4 Reactions

In general, the majority of particulate cadmium compounds which are commonly found in samples of workplace air are converted to water-soluble cadmium ions (Cd^{2+}) by the sample digestion procedure specified in 8.2.2. However, if there is any doubt about the effectiveness of this procedure for digestion of particulate cadmium compounds which could be present in the test atmosphere, investigate this before proceeding with the method (see 10.1).

5 Reagents

During the analysis, use only reagents of analytical grade, and only water as specified in 5.1.

5.1 Water, complying with the requirements for ISO 3696 grade 2 water (electrical conductivity less than 0,1 mS/m and resistivity greater than 0,01 MΩ·m at 25 °C).

5.2 Nitric acid, (HNO_3), concentrated, $\rho \approx 1{,}42$ g/ml, 69 % (*m/m*) to 71 % (*m/m*).

The concentration of cadmium shall be less than 0,01 µg/ml.

WARNING — Concentrated nitric acid is corrosive and oxidizing, and nitric acid fumes are irritant. Avoid exposure by contact with the skin or eyes, or by inhalation of fumes. Personal protective equipment (e.g. gloves, face shield or safety spectacles, etc.) must be used when working with the concentrated or diluted nitric acid, and concentrated nitric acid must be used in a fume hood.

5.3 Nitric acid, diluted 1 + 1.

Carefully add 500 ml of concentrated nitric acid (5.2) to 450 ml of water (5.1) in a 2 litre beaker. Swirl to mix, allow to cool and quantitatively transfer to a 1 000 ml one-mark volumetric flask (6.2.1.5). Dilute to the mark with water, stopper and mix thoroughly.

5.4 Nitric acid, diluted 1 + 9.

Pour approximately 800 ml of water (5.1) into a 1 000 ml one-mark volumetric flask (6.2.1.5). Carefully add 100 ml of concentrated nitric acid (5.2) to the flask and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly.

5.5 Cadmium stock standard solution, corresponding to 1 000 mg of Cd per litre.

5.5.1 Use a commercially available cadmium standard solution at a concentration of 1 000 mg/l. Observe the manufacturer's expiry date or recommended shelf-life.

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[1] To be published.

Alternatively, prepare a cadmium standard solution according to the procedure specified in 5.5.2.

5.5.2 Accurately weigh 1,000 g ± 0,001 g of cadmium metal, 99,9 % (*m/m*) of Cd, into a 50 ml beaker (6.2.1.1), add 20 ml of the nitric acid diluted 1 + 1 (5.3), cover with a watch glass (6.2.1.2) and heat to approximately 150 °C on the hotplate (6.2.4) in a fume hood until the metal is completely dissolved. Remove the beaker from the hotplate, allow to cool, quantitatively transfer the solution to a 1 000 ml one-mark volumetric flask (6.2.1.5), dilute to the mark with water (5.1), stopper and mix thoroughly.

This solution may be stored in a polypropylene bottle (6.2.2) for up to one year.

5.6 Cadmium working standard solution A, corresponding to 100 mg of Cd per litre.

Using a pipette (6.2.1.3), accurately add 10,0 ml of stock cadmium solution (5.5) to a 100 ml one-mark volumetric flask (6.2.1.5). Add 1 ml of concentrated nitric acid (5.2), dilute to the mark with water (5.1), stopper and mix thoroughly.

This solution may be stored in a polypropylene bottle (6.2.2) for up to one month.

5.7 Cadmium working standard solution B, corresponding to 1 mg of Cd per litre.

Using a pipette (6.2.1.3), accurately add 100 µl of cadmium stock solution (5.5) to a 100 ml one-mark volumetric flask (6.2.1.5). Add 1 ml of nitric acid (5.2), dilute to the mark with water (5.1), stopper and mix thoroughly.

This solution may be stored in a polypropylene bottle (6.2.2) for up to one month.

5.8 Matrix-modifier solution, corresponding to 1 g of $Mg(NO_3)_2{\cdot}6H_2O$ per litre and 20 g of $NH_4H_2PO_4$ per litre.

Weigh 0,100 g of magnesium nitrate hexahydrate $[Mg(NO_3)_2{\cdot}6H_2O]$ and 2,00 g of ammonium dihydrogen phosphate ($NH_4H_2PO_4$) into a 250 ml beaker (6.2.1.1). Add 50 ml of water (5.1) and swirl to dissolve. Add 10 ml of concentrated nitric acid (5.2), swirl to mix, and quantitatively transfer the solution to a 100 ml one-mark volumetric flask (6.2.1.5). Dilute to the mark with water, stopper and mix thoroughly.

5.9 Laboratory detergent solution, suitable for cleaning samplers and laboratory apparatus, diluted with water (5.1) according to the manufacturer's instructions.

5.10 Air, compressed and filtered.

5.11 Acetylene, in a cylinder.

5.12 Argon, supplied in a cylinder or as a cryogenic fluid.

NOTE 1 This gas is only required if analysis is carried out by electrothermal atomic absorption spectrometry (see 8.3.3.6).

6 Apparatus

6.1 Sampling equipment

6.1.1 Samplers, for collection of the inhalable fraction or the respirable fraction of airborne particles (see 7.1.1) as defined in ISO 7708, suitable for use with the cellulose ester membrane filters (6.1.2) and compatible with the sampling pumps (6.1.3) used.

NOTES

2 A number of different terms are used to describe samplers designed for collection of the inhalable fraction of airborne particles, for example, sampling heads, filter holders, filter cassettes and air monitoring cassettes.

3 In general, the collection characteristics of inhalable samplers are such that particulate material collected on the filter is the inhalable fraction of airborne particles, and any deposited on the internal surfaces of the sampler is not of interest. However, some samplers are designed such that airborne particles which pass through the entry orifice(s) constitute the inhalable fraction; in which case any particulate material deposited on the internal surfaces of the sampler is part of the sample. Certain samplers of this type incorporate an internal filter cassette or cartridge which may be removed from the sampler to enable this material to be easily recovered.

4 Cyclone samplers are typically used for collection of personal samples of the respirable fraction of airborne particles.

5 Samplers manufactured in non-conducting material have electrostatic properties which may influence representative sampling. Electrostatic influences should be reduced, where possible, by using samplers manufactured from conducting material.

6.1.2 Filters, soluble using the sample digestion procedure specified in 8.2.2, and with a retentivity not less than 99 % for particles of median aerodynamic diameter 0,3 µm (see ISO 7708:1995, subclause 2.2).

The cadmium content shall be less than 0,001 µg per filter.

NOTE 6 Cellulose ester membrane filters of 0,8 µm to 1,2 µm pore size are generally the most suitable. Cellulose (paper) filters can have a retentivity below 99 % and they are therefore unsuitable. Neither glass-fibre nor quartz-fibre filters are dissolved by the sample digestion procedure specified in 8.2.2, but this may be modified to permit their use (see note 26).

6.1.3 Sampling pumps, complying with the requirements of EN 1232, with an adjustable flow rate, incorporating a flowmeter or a flow-fault indicator, and capable of maintaining the appropriate flow rate (see 7.1.1) to within ± 5 % of the nominal value throughout the sampling period (see 7.1.2). For personal sampling, the pumps shall be capable of being worn by a person without impeding normal work activity. The pumps shall give a pulsation-free flow (if necessary, a pulsation damper shall be incorporated between the sampler and the pump, as near to the pump as possible).

NOTE 7 Flow-stabilized sampling pumps may be required to maintain the flow rate within the limits specified in 6.1.3.

6.1.4 Flowmeter portable, capable of measuring the appropriate flow rate (see 7.1.1) to within ± 5 %, and calibrated against a primary standard, i.e. a flowmeter of which the accuracy is traceable to national standards.

NOTES

8 The flowmeter incorporated in the sampling pump may be used provided that it has adequate sensitivity, that it has been calibrated against a primary standard with a loaded sampler in line, and that it is read whilst in a vertical orientation if it is of the supported float type. However, it is important to ensure that there are no leaks in the sampling train between the sampler and the flowmeter, since in this event a flowmeter in the sampling pump or elsewhere in line will give an erroneous flow rate.

9 A soap bubble flowmeter may be used as a primary standard, provided its accuracy is traceable to national standards.

10 If appropriate (see 7.1.3.2), the atmospheric temperature and pressure at which the flowmeter was calibrated should be recorded.

6.1.5 Ancillary equipment, including flexible plastics tubing of a diameter suitable for making a leakproof connection from the samplers (6.1.1) to the sampling pumps (6.1.3); belts or harnesses to which the sampling pumps can conveniently be fixed, unless they are small enough to fit in workers' pockets; flat-tipped forceps for loading and unloading filters into samplers; and filter-transport cassettes or similar, if required (see 7.4.1), to transport samples to the laboratory.

6.1.6 Thermometer, 0 °C to 50 °C, graduated in divisions of 1 °C or better, for measurement of atmospheric temperature (see 7.1.3).

6.1.7 Barometer, for measurement of atmospheric pressure (see 7.1.3).

6.2 Analytical or laboratory apparatus

Ordinary laboratory apparatus, and

6.2.1 Glassware, made of borosilicate glass 3.3 complying with the requirements of ISO 3585.

NOTE 11 It is preferable to reserve a set of glassware for analysis of cadmium by this method. Heavily contaminated glassware in general usage may not be satisfactorily cleaned using the procedure specified in 8.1.4.

6.2.1.1 Beakers, of capacity 50 ml for digestion of filters of the diameter used in the sampler (see 8.2.2) and for preparation of the cadmium stock standard solution (5.5.2); of capacity 250 ml for preparation of the matrix-modifier solution (5.8); and of capacity 2 litres for preparation of nitric acid diluted 1 + 1 (5.3).

6.2.1.2 Watch glasses, to fit the 50 ml beakers (6.2.1.1).

6.2.1.3 One-mark pipettes, complying with the requirements of ISO 648, as an alternative to piston-operated volumetric apparatus (6.2.3).

6.2.1.4 Measuring cylinders, of capacities between 10 ml and 1 litre.

6.2.1.5 One-mark volumetric flasks, of capacities between 10 ml and 1 000 ml, complying with the requirements of ISO 1042.

6.2.2 Polypropylene bottles, of capacity 1 litre.

NOTE 12 Bottles made of alternative plastics may be used, provided that they are suitable for the intended use (see 5.5.2, 5.6 and 5.7). However, the use of bottles made of coloured plastics should be avoided, since some contain cadmium pigments which can release cadmium when in contact with nitric acid solutions.

6.2.3 Piston-operated volumetric apparatus, complying with the requirements of ISO 8655-1 to ISO 8655-4. Automatic pipettes, as an alternative to one-mark pipettes (6.2.1.3) for preparation of the working standard solutions (5.6 and 5.7), working calibration solutions (see 8.4.1.1) and calibration solutions (see 8.3.1), and for dilution of samples with concentrations above the specific range (see 8.3.3.4 and 8.4.2.6); and dispensers for dispensing acids.

NOTE 13 If pipette tips made from coloured plastics are used, it is advisable to check with the manufacturer that they contain no cadmium pigments, since these can release cadmium in contact with nitric acid solutions.

6.2.4 Hotplate, thermostatically controlled, capable of maintaining a surface temperature of approximately 150 °C (see 8.1.2 and 8.2.2).

NOTE 14 The efficiency of thermostatting of hotplates is sometimes deficient, and the surface temperature can also vary considerably with position on a hotplate with a large surface area. It may therefore be useful to characterize the performance of the hotplate before use.

6.2.5 Atomic absorption spectrometer, fitted with an air-acetylene burner supplied with compressed air (5.10) and acetylene (5.11), and equipped with either a cadmium hollow cathode lamp or electrodeless discharge lamp. If electrothermal atomic absorption is to be carried out (see 8.3.3.6), the atomic absorption spectrometer shall be capable of carrying out simultaneous background correction at 228,8 nm, either by using a continuous source such as a deuterium lamp to measure non-specific attenuation (see ISO 6955:1982, subclause 5.1.5), or by using Zeeman or Smith-Hieftje background correction systems.

6.2.6 Electrothermal atomizer, fitted with a solid, pyrolytic graphite platform mounted in a pyrolytically coated graphite tube, supplied with argon (5.12) as a purge gas, and equipped with an autosampler capable of injecting microlitre volumes onto the platform.

NOTE 15 Some manufacturers of atomic absorption spectrometers use an alternative design of electrothermal atomizer to achieve a constant temperature environment during atomization, and some use aerosol deposition as a means of sample introduction. The use of such accessories is acceptable, but the performance of the method may be different from that given in 9.2.

6.2.7 Disposable autosampler cups, made of polystyrene or other suitable plastics, for use in the autosampler used with the electrothermal atomizer. Soak in nitric acid diluted 1 + 9 (5.4) before use.

NOTE 16 It is recommended to avoid the use of autosampler cups made of coloured plastics, since some contain cadmium pigments which can release cadmium in contact with nitric acid solutions.

6.2.8 Analytical balance, capable, of weighing to ± 0,1 mg.

6.2.9 Disposal gloves, impermeable, to avoid the possibility of contamination from the hands and to protect them from contact with toxic and corrosive substances. Poly(vinyl chloride) (PVC) gloves are suitable.

7 Sampling

7.1 Sampling procedure

7.1.1 Collection characteristics and flow rate

Select a sampler (6.1.1) suitable for collection of either the inhalable fraction or the respirable fraction of airborne particles, as defined in ISO 7708 (see note 17), and use at the flow rate at which the sampler exhibits the required collection characteristics.

NOTES

17 National occupational exposure limits for cadmium and cadmium compounds typically apply to the inhalable fraction of airborne particles, but some nations have established separate limit values for cadmium sulfide which apply to the respirable fraction of airborne particles. The sampler used should therefore be selected to meet national requirements.

18 Both inhalable and respirable samplers are typically used at flow rates of around 2 l/min (it is advisable to refer to the manufacturer's recommendations).

7.1.2 Sampling period

Select a sampling period of appropriate duration, using any available information about the work process and test atmosphere, so that the amount of cadmium collected is within the recommended working range of the method.

NOTE 19 In order to estimate a sampling period of appropriate duration it is necessary to consider the flow rate used (see 7.1.1) and the anticipated concentration of cadmium in the test atmosphere. When low cadmium-in-air concentrations are anticipated, the lower limit of the working range of the method (see 9.3.2) should be taken into consideration. For example, to determine cadmium in air at a concentration of 5 µg/m³ using flame atomic absorption spectrometry, the minimum sampling time at a flow rate of 2 l/min is 50 min. When high cadmium-in-air concentrations are anticipated, the sampling time should not be long enough to risk overloading the filter with particulate matter.

7.1.3 Temperature and pressure effects

7.1.3.1 Consider whether it is necessary to recalculate the mass concentration of cadmium in air to reference conditions of temperature and pressure in order to comply with national standards and regulations (see ISO 8756). If appropriate, measure and record the atmospheric temperature and pressure throughout the sampling period (see 7.3.2, 7.3.3 and 7.3.5) and use the equation given in 9.1.3 to apply the necessary correction.

NOTE 20 Cadmium-in-air concentrations are generally stated for the actual environmental conditions (temperature, pressure) at the workplace.

7.1.3.2 The indicated flow rate of certain types of flowmeter is dependent upon temperature and pressure. Therefore, refer to the manufacturer's directions for the particular flowmeter used, and consider whether it is necessary to make a correction to take into account any difference between the atmospheric temperature and pressure at the time of calibration of the flowmeter and at the time of sampling. Make such a correction if it is considered possible that an error of greater than ± 5 % will be introduced by not doing so. If a correction is to be made, measure and record the atmospheric temperature and pressure at which the flowmeter (6.1.4) was calibrated.