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

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 146, Air Quality, Subcommittee SC 2, Workplace atmospheres.

This second edition cancels and replaces the first edition (ISO 11174:1996), which has been technically revised.

The main changes compared to the previous edition are as follows:

- A reference for handling of sampler wall deposits has been added.
- References and definitions have been updated.
- Additional editorial changes have been made.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

The health of workers in many industries, such as mining, metal refining, battery manufacture, foundries, electronics and construction, is at risk through exposure by inhalation of particulate cadmium and cadmium compounds. Industrial hygienists and other public health professionals need to determine the effectiveness of measures taken to control workers' exposure, and this is generally achieved by making workplace air measurements. This document provides a method for making valid exposure measurements for cadmium. It will be of benefit to: agencies concerned with health and safety at work; industrial hygienists and other public health professionals; analytical laboratories; industrial users and workers of metals and metalloids, etc.

It has been assumed in the drafting of this document that the execution of its provisions, and the interpretation of the results obtained, is entrusted to appropriately qualified and experienced people.

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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^[1]. 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 document 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 10.2.2 has been validated^[2,3] for a selection of cadmium compounds and pigments and glass enamels containing cadmium.

The analytical method has been validated^[2] 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^[3]. 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 stationary sampling.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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.

ISO 648, *Laboratory glassware — Single-volume pipettes*

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

ISO 3585, *Borosilicate glass 3.3 — Properties*

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

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

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

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

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

ISO 8655-5, *Piston and/or plunger operated volumetric apparatus (POVA) — Part 5: Dispensers*

ISO 8655-6, *Piston and/or plunger operated volumetric apparatus (POVA) — Part 6: Gravimetric methods for the determination of measurement error*

ISO 13137, *Workplace air quality — Pumps for personal sampling of chemical agents — Requirements and test methods*

ISO 15202-1, *Workplace air — Determination of metals and metalloids in airborne particulate matter by inductively coupled plasma atomic emission spectrometry — Part 1: Sampling*

ISO 15202-2:2020, *Workplace air — Determination of metals and metalloids in airborne particulate matter by inductively coupled plasma atomic emission spectrometry — Part 2: Sample preparation*

ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories*

ISO 18158, *Workplace air — Terminology*

ISO 20581, *Workplace air — General requirements for the performance of procedures for the measurement of chemical agents*

ISO 21832, *Workplace air — Metals and metalloids in airborne particles — Requirements for evaluation of measuring procedures*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 18158, ISO 6955 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <https://www.electropedia.org/>

3.1 exposure by inhalation

situation in which a chemical agent is present in air which is inhaled by a person

3.2 sample dissolution

process of obtaining a solution containing all analytes of interest from a sample, which might or might not involve complete dissolution of the sample

[SOURCE: ISO 15202-2:2020, 3.1]

3.3 sample solution

solution prepared from a sample by the process of *sample dissolution* (3.2)

[SOURCE: ISO 15202-2:2020, 3.2]

3.4 test solution

blank solution or *sample solution* (3.3) that has been subjected to all operations required to bring it into a state in which it is ready for analysis

[SOURCE: ISO 15202-2:2020, 3.3, modified: Note 1 to entry deleted]

4 Principle

4.1 Particulate cadmium and cadmium compounds are collected by drawing a measured volume of air through a sampling substrate (8.2), such as a filter or foam, mounted in a sampler (8.1) designed to collect either the inhalable fraction of airborne particles or the respirable fraction of airborne particles, as appropriate.

4.2 A test solution is prepared by treating the sampling substrate (8.2) and collected sample with 5 ml of nitric acid diluted 1 + 1 (7.3), heating on a hotplate until about 1 ml of concentrated nitric acid (7.2) solution remains, allowing the solution to cool and then diluting to 10 ml with water (7.1).

4.3 The test solution is analysed for cadmium by aspirating into the oxidizing air/acetylene flame of an atomic absorption spectrometer (8.6.5) 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).

4.4 For accurate determination when the concentration of cadmium in the solution is low, the analysis can 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).

5 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 10.2.2. 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. For instance, it is possible that other digestion methods described in ISO 15202-2:2020 will be suitable.

6 Requirement

The measuring procedure shall comply with any relevant international, European or national standard which specifies performance requirements for procedures for measuring chemical agents in workplace air (e.g. ISO 20581, ISO 21832).

7 Reagents

During the analysis, use only reagents of analytical grade, and only water as specified in 7.1.

7.1 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 $\text{M}\Omega\cdot\text{m}$ at 25 °C).

The concentration of cadmium in the water shall be less than 0,01 $\mu\text{g}/\text{ml}$.

It is recommended that the water used be obtained from a water purification system that delivers ultrapure water having a resistivity greater than 0,18 $\text{M}\Omega\cdot\text{m}$ (usually expressed by manufacturers of water purification systems as 18 $\text{M}\Omega\cdot\text{cm}$).

7.2 Nitric acid (HNO_3), concentrated, $\rho = 1,42 \text{ g}/\text{ml}$, 69 % (m/m) to 71 % (m/m).

The concentration of cadmium shall be less than 0,01 $\mu\text{g}/\text{ml}$.

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) must be used when working with the concentrated or diluted nitric acid, and concentrated nitric acid must be used in a fume hood.

7.3 Nitric acid, diluted 1 + 1.

Carefully add 500 ml of concentrated nitric acid (7.2) to 450 ml of water (7.1) in a 2 litre beaker. Swirl to mix, allow to cool and quantitatively transfer to a 1 000 ml one-mark volumetric flask (8.6.1.7). Dilute to the mark with water, stopper and mix thoroughly.

7.4 Nitric acid, diluted 1 + 9.

Pour approximately 800 ml of water (7.1) into a 1 000 ml one-mark volumetric flask (8.6.1.7). Carefully add 100 ml of concentrated nitric acid (7.2) to the flask and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly.

7.5 Hydrofluoric acid (HF), concentrated, $\rho \approx 1,16$ g/ml (about 48 % mass fraction), if required (see 10.2.2), for digestion of samples containing lead silicates.

The concentration of cadmium in the HF shall be less than 0,1 $\mu\text{g/ml}$.

WARNING — Concentrated hydrofluoric acid and hydrogen fluoride vapour are extremely toxic and intensely corrosive. Diluted hydrofluoric acid can also cause serious and painful burns, and it is possible that these burns will not be felt until up to 24 h after contact. Avoid exposure by contact with the skin or the eyes, or by inhalation of the vapour. Use of personal protection (e.g. impermeable gloves, face shield or safety glasses) is essential when working with concentrated or diluted hydrofluoric acid, and concentrated hydrofluoric acid should be used in a fume hood. It is essential that hydrofluoric acid antidote gel containing calcium gluconate is readily available to workers, both during and for 24 h after use of hydrofluoric acid.

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

7.6.1 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.

Alternatively, prepare a cadmium standard solution according to the procedure specified in 7.6.2.

7.6.2 Accurately weigh 1 000 g \pm 0,001 g of cadmium metal, 99,9 % of Cd, into a 50 ml beaker (8.6.1.1), add 20 ml of the nitric acid diluted 1 + 1 (7.3), cover with a watch glass (8.6.1.4) and heat to approximately 150 °C on the hotplate (8.6.4) 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 (8.6.1.7), dilute to the mark with water (7.1), stopper and mix thoroughly.

This solution can be stored in a polypropylene bottle (8.6.2.2) for up to one year.

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

Using a pipette (8.6.3.1), accurately add 10,0 ml of stock cadmium solution (7.6) to a 100 ml one-mark volumetric flask (8.6.1.7). Add 1 ml of concentrated nitric acid (7.2), dilute to the mark with water (7.1), stopper and mix thoroughly.

This solution can be stored in a polypropylene bottle (8.6.2.2) for up to one month.

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

Using a pipette (8.6.3.1), accurately add 100 μl of cadmium stock solution (7.6) to a 100 ml one-mark volumetric flask (8.6.1.7). Add 1 ml of nitric acid (7.2), dilute to the mark with water (7.1), stopper and mix thoroughly.

This solution can be stored in a polypropylene bottle (8.6.2.2) for up to one month.

7.9 Matrix-modifier solution, corresponding to 10 g of $\text{NH}_4\text{H}_2\text{PO}_4$ per litre of water (6.1).

Weigh 1,00 g of ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) into a 250 ml beaker (8.6.1.1). Add 50 ml of water (7.1) and swirl to dissolve. Add 10 ml of concentrated nitric acid (7.2), swirl to mix, and quantitatively transfer the solution to a 100 ml one-mark volumetric flask (8.6.1.7). Dilute to the mark with water, stopper and mix thoroughly.

If modifications are needed to optimize the matrix-modifier solution, these modifications should be described in the test report (Clause 13).

7.10 Laboratory detergent solution, suitable for cleaning samplers (8.1) and laboratory apparatus, diluted with water (7.1) according to the manufacturer's instructions.

7.11 Air, high-purity, compressed and filtered.

7.12 Acetylene, in a compressed gas cylinder.

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

This gas is required if analysis is carried out by electrothermal atomic absorption spectrometry (see 10.3.3.6).

8 Apparatus

8.1 Samplers, for collection of the inhalable fraction or the respirable fraction of airborne particles (see 9.1.1) as defined in ISO 7708, suitable for use with the sampling substrates (8.2) and compatible with the sampling pumps (8.3) used.

NOTE 1 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 (see ISO 15202-1).

NOTE 2 In general, the collection characteristics of inhalable samplers are such that particulate material collected on the filter sampling substrate is the inhalable or respirable 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 or respirable 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 can be removed from the sampler to enable this material to be easily recovered. See ASTM D8358^[4] for further information on inclusion of sampler internal wall deposits.

NOTE 3 Cyclone samplers are typically used for collection of personal samples of the respirable fraction of airborne particles.

NOTE 4 Samplers manufactured in non-conducting material have electrostatic properties which can influence representative sampling. Samplers manufactured from conducting material can reduce electrostatic influences.

8.2 Sampling substrates, such as filters or foams, soluble using the sample digestion procedure specified in 10.2.2, and with a retentivity not less than 99 % for particles of median aerodynamic diameter 0,3 μm (see ISO 7708).

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

NOTE Mixed 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 are therefore unsuitable. Neither glass-fibre nor quartz-fibre filters are dissolved by the sample digestion procedure specified in 10.2.2, but this can be modified to permit their use. Furthermore, such filters can have high metal background which can cause interference in highly sensitive analysis.