INTERNATIONAL STANDARD

ISO 11174

First edition
1996-04-15

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

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.

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.

International Organization for Standardization
Case Postale 56 • CH-1211 Genève 20 • Switzerland

Printed in Switzerland

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.*

---

[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.

---

[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/m^3 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.

NOTE 21 An example of temperature and pressure correction for the indicated flow rate is given in 9.1.2, for a flowmeter of variable area with constant pressure drop.

7.2 Preparation of sampling equipment

Perform the following in an area where cadmium contamination is known to be low.

7.2.1 Clean the samplers (6.1.1) before use. Disassemble the samplers, soak in laboratory detergent solution (5.9), rinse thoroughly with water (5.1), wipe with absorptive tissue and allow to dry before reassembly.

7.2.2 Load the filters (6.1.2) into clean, dry samplers (7.2.1) using clean, flat-tipped forceps (6.1.5). Connect each loaded sampler to a sampling pump (6.1.3) using plastics tubing (6.1.5), ensuring that no leaks can occur. Switch on the sampling pump, attach the calibrated flowmeter (6.1.4) to the sampler so that it measures the flow through the sampler inlet orifice(s), and set the appropriate flow rate (see 7.1.1) with an accuracy of ± 5 %. Switch off the sampling pump and seal the sampler with its protective cover or plug to prevent contamination with cadmium during transport to the sampling position.

NOTE 22 It might be necessary to warm up certain types of sampling pump (it is recommended to refer to the manufacturer's instructions).

7.3 Collection of samples

7.3.1 For personal sampling, fix the sampler to the lapel of the worker, in the breathing zone and as close to the mouth and nose as is reasonably practicable. Then, either place the sampling pump in a convenient pocket or attach it to the worker in a manner that causes minimum inconvenience, for example, to a belt (6.1.5) around the waist. For fixed-location sampling, position the sampler at the sampling site.

NOTE 23 The breathing zone has been defined in EN 1540 (reference [5] in annex B) as the space around the worker's face from where he takes his breath. For technical purposes, a more precise definition can be provided, as follows: hemisphere (generally accepted to be 0,3 m in radius) extending in front of the human face, centred on the midpoint of a line joining the ears; the base of the hemisphere is a plane through this line, the top of the head and the larynx.

7.3.2 When ready to begin sampling, remove the protective cover or plug from the sampler and switch on the sampling pump. Record the time at the start of the sampling period and, if the sampling pump has an elapsed time indicator, set this to zero. If appropriate (see 7.1.3.1), measure the atmospheric temperature and pressure at the start of the sampling period using the thermometer (6.1.6) and barometer (6.1.7) and record the measured values.

7.3.3 Since it is possible for a filter to become clogged, monitor the performance of the sampler frequently, a minimum of once per hour. Measure the flow rate with an accuracy of ± 5 % using the calibrated flowmeter (6.1.4) and, if appropriate (see 7.1.3.1), measure the atmospheric temperature using the thermometer (6.1.6) and the atmospheric pressure using the barometer (6.1.7). Record the measured values.

NOTE 24 Regular observation of the flow-fault indicator is an acceptable means of ensuring that the flow rate of a flow-stabilized sampling pump is maintained satisfactorily, provided that the flow-fault indicator indicates malfunction when the flow rate is outside ± 5 % of the nominal value.

7.3.4 Terminate sampling and consider the sample to be invalid if the flow rate is not maintained to within ± 5 % of the nominal value throughout the sampling period.

7.3.5 At the end of the sampling period (see 7.1.2), measure the flow rate with an accuracy of ± 5 % using the calibrated flowmeter (6.1.4), switch off the sampling pump and record the flow rate and the time. Also observe the reading on the elapsed time indicator, if fitted, and consider the sample to be invalid if the reading on the elapsed time indicator and the timed interval between switching the sampling pump on and off do not agree to within ± 5 %, since this may suggest that the sampling pump has not been operating throughout the sampling period. Reseal the sampler with its protective cover or plug and disconnect it from the sampling pump. If appropriate (see 7.1.3.1), measure the atmospheric temperature and pressure at the end of the sampling period using the thermometer (6.1.6) and barometer (6.1.7) and record the measured values.

7.3.6 Carefully record the sample identity and all relevant sampling data (see clause 11). Calculate the mean flow rate by averaging the flow-rate measurements taken throughout the sampling period, and, if appropriate (see 7.1.3.1), calculate the mean atmospheric temperature and pressure. Calculate the volume of air sampled, in litres, at atmospheric temperature and pressure, by multiplying the mean flow rate, in litres per minute, by the sampling time, in minutes.

7.3.7 With each batch of 10 samples, submit for analysis two unused filters from the same lot as used for sample collection. Subject these blank filters to exactly the same handling procedure as the samples, but do not draw air through them.

7.4 Transportation

Perform the following in an area where cadmium contamination is known to be low.

7.4.1 For samplers which collect the required fraction of airborne particles on the filter (see note 3), remove the filter from each sampler using clean flat-tipped forceps (6.1.5), place in a labelled filter-transport cassette (6.1.5) and close with a lid.

7.4.2 For samplers which have an internal filter cassette (see note 3), remove the filter cassette from each sampler, fasten with the transport clip supplied by the manufacturer, and label appropriately.

7.4.3 For samplers designed such that airborne particles which pass through the entry orifice(s) constitute the inhalable fraction, but which do not have an internal filter cassette (see note 3), and for samplers of the disposable cassette type, transport samples to the laboratory in the samplers in which they were collected.

7.4.4 Transport the filter-transport cassettes (see 7.4.1), sampler filter cassettes (see 7.4.2) or samplers (see 7.4.3) in a container which has been designed to prevent damage to the samples in transit and which has been labelled to assure proper handling.

8 Procedure for analysis

8.1 Cleaning of glassware and polypropylene bottles

8.1.1 Before use, clean all glassware to remove any residual grease or chemicals, by soaking in laboratory detergent solution (5.9) and then rinsing thoroughly with water (5.1).

8.1.2 After initial cleaning (see 8.1.1), clean all beakers used in the sample digestion procedure specified in 8.2.2 with hot nitric acid. Fill to one-third capacity with concentrated nitric acid (5.2), cover with a watch glass (6.2.1.2), heat to approximately 150 °C on the hotplate (6.2.4) in a fume hood for 1 h, allow to cool, and then rinse thoroughly with water (5.1).

8.1.3 After initial cleaning (see 8.1.1), clean all glassware other than beakers used in the sample digestion procedure specified in 8.2.2, by soaking in nitric acid diluted 1 + 9 (5.4) for at least 24 h, and then rinsing thoroughly with water (5.1).

8.1.4 Thoroughly rinse glassware which has been previously subjected to the entire cleaning procedure specified in 8.1.1, 8.1.2 and 8.1.3, and which has been reserved for analysis of cadmium by this method, first with nitric acid diluted (5.4) 1 + 9 and then with water (5.1).

8.1.5 Before use, clean the polypropylene bottle (6.2.2) by soaking in nitric acid diluted 1 + 9 (5.4) for at least 24 h and then rinsing thoroughly with water (5.1).

8.2 Preparation of sample solutions and blank test solutions

8.2.1 Open the filter-transport cassettes (see 7.4.1), sampler filter cassettes (see 7.4.2) or samplers (see 7.4.3) and transfer each filter to an individual clean, labelled 50 ml beaker (6.2.1.1) using clean, flat-tipped forceps (6.1.5). If the sampler used was of a type in which airborne particles deposited on the internal surfaces of the sampler filter cassette or sampler forms part of the sample (see note 3), wash any particulate material adhering to the internal surfaces into the beaker using a minimum volume of water (5.1). Follow the same procedure for the blank filters (see 7.3.7).

8.2.2 Add 5 ml of nitric acid diluted 1 + 1 (5.3) to each beaker, partially cover with a watch (6.2.1.2), and heat to approximately 150 °C (see note 25) on the hotplate (6.2.4) in a fume hood, until the filter has dissolved and the volume has been reduced to approximately 1 ml. Then remove the beakers from the hotplate and allow the solutions to cool.

NOTES

25 The exact temperature of the hotplate is not critical. A temperature of 150 °C is used because it is high enough to enable the liquid to be evaporated at an acceptable rate, whilst not being high enough to evaporate the liquid at such a rate that there is a significant risk of inadvertently evaporating all the solution and baking the residue.

26 If glass-fibre or quartz-fibre filters are used (see note 6), it is necessary to use polytetrafluoroethylene (PTFE) laboratory apparatus and to add hydrofluoric acid to dissolve the filters before addition of nitric diluted 1 + 1. In such circumstances, the procedure described in 8.3.1 should be modified to prepare calibration solutions in hydrofluoric acid diluted 1 + 9 (see note 27). Furthermore, if test solutions are analysed using flame atomic absorption spectrometry, it is necessary to use a nebulizer that is resistant to attack by hydrofluoric acid solutions.

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

8.2.3 Carefully rinse the watch glass and the sides of each beaker with water (5.1) and transfer each solution quantitatively to a 10 ml one-mark volumetric flask (6.2.1.5).

If necessary, remove any undissolved particulate matter by filtering the solution through a cellulose (paper) filter which has been prewashed with nitric acid diluted 1 + 9 (5.4) and then with water (5.1).

Finally, dilute to the mark with water (5.1), stopper and mix thoroughly.

8.3 Analysis by flame atomic absorption spectrometry

NOTE 27 Laboratory experiments (see reference [2] in annex B) have shown that flame atomic absorption measurements of cadmium are not affected significantly by variation in nitric acid concentrations with the range 1 + 19 nitric acid to 1 + 3 nitric acid. However, it is good laboratory practice to match sample and standard matrices as far as is reasonably practicable.

8.3.1 Preparation of calibration solutions

Prepare at least six calibration solutions, including a zero-member calibration solution (see ISO 6955:1982, subclause 5.4.7), to cover the range 0 µg of Cd per millilitre to 1,0 µg of Cd per millilitre. Add 20 ml of nitric acid diluted 1 + 1 (5.3) to separate, labelled 100 ml one-mark volumetric flasks (6.2.1.5). Using a pipette (6.2.1.3), accurately add the appropriate volume of the cadmium working standard solution A (5.6) to each flask, dilute to the mark with water (5.1), stopper and mix thoroughly.

Prepare fresh calibration solutions each week.

NOTE 28 The range of the set of calibration solutions is given as a guide. The upper limit of the working range depends upon which wavelength is used, and it is also governed by instrumental factors which affect sensitivity and the linearity of the calibration. Accordingly, the range of the set of calibration solutions may be varied, but when making any changes it should be ensured that the response of the spectrometer over the alternative range of concentrations selected is such that it complies with the limitations on curvature indicated in note 31.

8.3.2 Calibration

8.3.2.1 Set-up the atomic absorption spectrometer (6.2.5) to make absorbance measurements at a wavelength of 228,8 nm using an oxidizing air/acetylene flame. Use background correction to correct for non-specific attenuation (see ISO 6955:1982, subclause 5.1.5), if appropriate. Follow the manufacturer's recommendations for specific parameters for the operation of instruments.

NOTE 29 Use of the 228,8 nm cadmium line is specified in this International Standard since the only alternative is the 326,1 nm cadmium line, which exhibits very much lower sensitivity. The sensitivity, defined as the concentration required to produce a signal of 1 % absorbance or 0,004 4 absorbance units, is about 0,02 µg of Cd per millilitre for the 228,8 nm cadmium line.

8.3.2.2 Adjust the spectrometer zero whilst aspirating the zero-member calibration solution (8.3.1) into the flame. (Repeat this procedure regularly throughout the calibration and readjust the zero if the baseline drifts.) Then aspirate the calibration solutions (8.3.1) into the flame and make absorbance measurements for each solution.

NOTE 30 Use of an autosampler to present the calibration solutions to the atomic absorption spectrometer may improve the precision of the absorbance measurements and reduce the volume of solution consumed.

8.3.2.3 For instruments controlled by a microprocessor or personal computer, use a suitable algorithm to generate the calibration function. For instruments without this possibility, prepare a calibration graph by plotting the absorbance of the calibration solutions versus the concentration of cadmium, in micrograms per millilitre, in the respective solutions.

NOTE 31 In general, it is best to work in the linear range of an atomic absorption calibration, where absorbance is proportional to the concentration of cadmium in solution. However, a certain amount of curvature can be tolerated, but ideally the slope of the top 20 % of the calibration curve should be not less than 70 % of the slope of the bottom 20 % calculated in the same manner. If the calibration obtained does not comply with these limitations on curvature, it is advisable to prepare a new set of calibration standards with cadmium concentrations lower than those recommended in 8.3.1.

8.3.3 Determination

8.3.3.1 Adjust the spectrometer zero whilst aspirating the zero-member calibration solution (see 8.3.1) into the flame. (Repeat this procedure regularly throughout the determination and readjust the zero if the baseline drifts.) Then aspirate the sample solution and blank test solution (see 8.2.3) into the flame and make absorbance measurements for each solution. For instruments controlled by a microprocessor or personal computer, use the calibration function (see 8.3.2.3) to calculate the concentration of cadmium in the sample solutions, and obtain a direct read-out of the results in concentration units. For instruments without this possibility, determine the concentration of cadmium in the sample solutions from the calibration graph (see 8.3.2.3).

NOTE 32 Use of an autosampler to present the sample solutions to the atomic absorption spectrometer may improve the precision of the results and reduce the volume of solution used.

8.3.3.2 Aspirate a mid-range calibration solution after each five to ten sample and make an absorbance measurement. If this indicates that the sensitivity has changed by more than ± 5 %, take one of the following corrective measures: either use the available software facilities of the microprocessor or personal computer to correct for the sensitivity change (reslope facility); or suspend analysis and recalibrate the spectrometer as specified in 8.3.2.2 and 8.3.2.3. In both cases, reanalyse the sample solutions which were analysed during the period in which the sensitivity change occurred.

8.3.3.3 If low concentrations of cadmium are found, consider using scale expansion, since this may, in some instances, improve the precision of measurements made near the detection limit.

8.3.3.4 If high concentrations of cadmium are found, dilute the sample solutions (see 8.2.3) to bring the concentration within the calibration range. Make all dilutions so that the final nitric acid concentration is 1 + 9, and record the dilution factor F.

8.3.3.5 Calculate the mean cadmium concentration in the blank test solutions.

8.3.3.6 If the concentration of cadmium in the sample solutions (see 8.2.3) is less than 0,05 µg/ml, consider repeating the analysis using electrothermal atomic absorption spectrometry (see 8.4), since this technique gives more precise measurements at low concentrations.

8.4 Analysis by electrothermal atomic absorption spectrometry

NOTE 33 Cadmium is present at a low level in the environment and therefore it is essential that strict standards of cleanliness are observed to avoid contamination of laboratory apparatus. This is particularly important when carrying out electrothermal atomic absorption spectrometry, since the technique exhibits a very low detection limit. It should be ensured that all glassware is cleaned thoroughly before use in accordance with 8.1, and that autosampler cups (6.2.7) are stored in nitric acid diluted 1 + 9 (5.4) until required.

8.4.1 Preparation of working calibration solutions

8.4.1.1 Prepare a working calibration solution at a concentration of 2,5 ng of Cd per millilitre. Using a pipette (6.2.1.3), accurately add 250 µl of cadmium working standard solution B (5.7) to a 100 ml one-mark volumetric flask (6.2.1.5). Add about 50 ml of water (5.1) and 20 ml of nitric acid diluted 1 + 1 (5.3), and swirl to mix. Allow to cool, dilute to the mark with water (5.1), stopper and mix thoroughly.

Prepare a fresh solution each week.

8.4.1.2 Prepare a working calibration blank solution following the procedure in 8.4.1.1, but omitting the 250 µl of cadmium working standard solution B (5.7).

Prepare a fresh solution each week.

8.4.2 Calibration and determination

8.4.2.1 Set up the atomic absorption spectrometer (6.2.5) and electrothermal atomizer (6.2.6) to determine cadmium at a wavelength of 228,8 nm, using background correction to correct for non-specific attenuation (ISO 6955:1982, subclause 5.1.5). Follow the manufacturer's recommendations for specific operating parameters.

NOTE 34 The operating parameters for electrothermal atomic absorption spectrometry vary considerably between different instruments, much more so than for flame atomic absorption spectrometry. Typical operating parameters are given in annex A. The characteristic mass, defined as the number of picograms required to give 0,004 4 absorbance seconds, is typically about 1 pg for cadmium. This is equivalent to a sample solution concentration of 0,05 ng of Cd per millilitre of cadmium for a 20 µl sample solution injection volume.

8.4.2.2 Program the autosampler to prepare matrix-modified reference solutions, sample solutions and blank test solutions *in situ* on a pyrolytic graphite platform mounted in the pyrolytically coated graphite tube of the electrothermal atomizer. Prepare at least six matrix-modified calibration solutions to cover the range 0 ng of Cd per millilitre to 2,5 ng of Cd per millilitre using the working calibration solution (see 8.4.1.1), the working calibration blank solution (see 8.4.1.2) and the matrix-modifier solution (5.8). Prepare matrix-modified sample and blank test solutions using the sample solutions, blank test solutions (see 8.2.3) and matrix-modifier solution (5.8). (See table A.2 for typical autosampler injection volumes.)

NOTES

35 The procedure described above may be varied to accommodate the use of electrothermal atomizers of alternative design (see note 15).

36 Matrix-modified calibration and sample solutions may be prepared in one-mark volumetric flasks (6.2.1.5) as an alternative to preparation *in situ* using the autosampler.

37 Sample solutions should be diluted (see 8.4.2.6) before analysis by electrothermal atomic absorption spectrometry (see 8.3.3.6), if results obtained by flame atomic absorption spectrometry indicate that the cadmium concentration is above the upper limit of the calibration range for electrothermal atomic absorption spectrometry (see 8.4.2.2).

8.4.2.3 Set up the analytical sequence in the microprocessor or personal computer. Specify an appropriate number of replicate analyses for each solution, and insert a calibration blank solution and a mid-range calibration solution after each five to ten sample solutions to monitor for baseline drift and sensitivity change, respectively.

8.4.2.4 Place the working calibration solution (see 8.4.1.1), the working calibration blank solution (see 8.4.1.2), the matrix-modifier solution (5.8), and the sample solutions (see 8.2.3) in separate acid-washed autosampler cups (6.2.7), and position as appropriate in the autosampler carousel. Analyse the matrix-modified calibration and sample solutions, using the microprocessor or personal computer software to generate a calibration and obtain a direct read-out of sample and blank results in nanograms of cadmium per millilitre.

8.4.2.5 If significant baseline drift is observed during the course of the analysis, or if the sensitivity has changed by more than ± 5 %, take one of the following appropriate corrective measures: either use the available software facilities of the microprocessor or personal computer to correct the sensitivity change (reslope facility); or suspend analysis and recalibrate the spectrometer as specified in 8.4.2.4. In both cases, reanalyse the sample solutions which were analysed during the period in which the sensitivity change occurred.

8.4.2.6 If concentrations of cadmium above the upper limit of the calibration range (see 8.4.2.2) are found, dilute the sample solutions to bring them within the calibration range, and repeat the analysis. Make all dilutions so that the final nitric acid concentration is 1 + 9, and record the dilution factor F.

38 Alternatively, the cadmium concentration may be brought within the calibration range by using a reduced aliquot of sample solution (see table A.2).

8.4.2.7 Calculate the mean cadmium concentration in the blank test solutions.

8.5 Estimation of the instrumental detection limit

8.5.1 Estimate the instrumental detection limit (see note 40) under the working analytical conditions, following the procedure specified in 8.5.2 and 8.5.3, and repeat this exercise whenever these conditions are changed.

8.5.2 Prepare a reference solution at a concentration of 0,01 µg of Cd per millilitre for flame atomic absorption spectrometric analysis and 0,1 ng of Cd per millilitre for electrothermal atomic absorption spectrometric analysis by diluting working cadmium standard solution B (5.7). Make this dilution so that the final nitric acid concentration is 1 + 9.

8.5.3 Make at least 20 absorbance measurements on the reference solution (see 8.5.2) and calculate the instrumental detection limit using standard statistical methods.

NOTES

39 The limit of detection of an atomic absorption method is defined in ISO 6955:1982, subclause 6.2.3, as the concentration of analyte for which the absorbance has a value equal to k times that of the standard deviation of a series of readings measured on a solution, the concentration of which is distinctly detectable above, but close to, that of the blank (k is generally taken as either 2 or 3). For the purposes of this International Standard, k should be taken as 3.

40 The limit of detection calculated from results obtained using the procedure specified in 8.5.2 and 8.5.3 is an instrumental detection limit. This is of use in identifying changes in instrument performance, but it is not a detection limit of the method and is likely to be unrealistically low because it only takes into account the variability between instrumental readings. Determinations made on one solution do not take into consideration variability from the matrix or sample variability. A more realistic detection limit for the analytical procedure specified in this International Standard may be obtained by making measurements on at least 10 blank test solutions, i.e. solutions of blanks (see 7.3.7). The standard deviation of such measurements, made over a longer time interval than between successive calibrations, may be used to obtain an estimate of the detection limit of the method.

9 Expression of results

9.1 Calculations

9.1.1 Calculate the mass concentration of cadmium in the air sample, ρ_{Cd}, in milligrams per cubic metre (however, see note 41), at ambient conditions, using the equation

$$\rho_{Cd} = \frac{\left(\rho_{Cd,1} \cdot V_1 \cdot F\right) - \left(\rho_{Cd,0} \cdot V_0\right)}{V}$$

where

$\rho_{Cd,0}$ is the mean concentration of cadmium, in micrograms per millilitre, in the blank test solutions (see 8.3.3.5 or 8.4.2.7);

$\rho_{Cd,1}$ is the concentration of cadmium, in micrograms per millilitre, in the sample solution (see 8.3.3.1 or 8.4.2.4);

V is the volume, in litres, of the air sample (see 9.1.2);

V_0 is the volume, in millilitres, of the blank test solution, i.e. 10 ml (see 8.2.3);

V_1 is the volume, in millilitres, of the sample solution, i.e. 10 ml (see 8.2.3);

F is the dilution factor used in 8.3.3.4 or 8.4.2.6 (F = 1 in the absence of dilution.

41 For low concentrations of cadmium-in-air determined by electrothermal atomic absorption spectrometry, it is recommended to calculate results in micrograms per cubic metre by using solution concentrations in nanograms per millilitre in the above equation.

9.1.2 In some instances, it is necessary to apply a temperature and pressure correction for the indicated sampling flow rate (see 7.1.3.2). A typical example of when such a correction is necessary is when the sampling pump used incorporates a flowmeter of variable area with constant pressure drop, which was calibrated and used to measure the flow rate in 7.3.2, 7.3.3 and 7.3.5. In this instance, use the following equation to calculate the volume of air samples

$$V_{\text{corr}} = q_V \cdot t \sqrt{\frac{p_1 \cdot T_2}{p_2 \cdot T_1}}$$

where

V_{corr}	is the corrected volume, in litres;
q_V	is the mean flow rate, in litres per minute;
t	is the sampling time, in minutes;
p_1	is the atmospheric pressure, in kilopascals, during calibration of the sampling pump flowmeter;
p_2	is the mean atmospheric pressure, in kilopascals, during the sampling period;
T_1	is the temperature, in kelvins, during calibration of the sampling pump flowmeter;
T_2	is the mean temperature, in kelvins, during the sampling period.

Any other flowmeter may also require correction for variation in temperature and pressure. Follow the manufacturer's instructions for such corrections.

9.1.3 If appropriate (see 7.1.3.1), calculate the mass concentration of cadmium in the air sample at reference temperature and pressure (273 K and 101,3 kPa, respectively), $\rho_{\text{Cd, corr}}$, using the equation

$$\rho_{\text{Cd, corr}} = \rho_{\text{Cd}} \times \frac{101{,}3\, T_2}{p_2 \times 273}$$

where

ρ_{Cd}	is the mass concentration of cadmium in the air sample, in milligrams per cubic metre, at ambient conditions, as calculated in 9.1.1;
T_2	is the mean temperature, in kelvins, during the sampling period;
p_2	is the mean atmospheric pressure, in kilopascals, during the sampling period;
273	is the reference temperature, in kelvins;
101,3	is the standard atmospheric pressure, in kilopascals.

9.2 Performance of the method

9.2.1 Laboratory experiments indicate that the analytical method does not exhibit significant bias. The mean analytical recovery for spiked filters in the range 0,15 µg to 96 µg of cadmium was determined (see reference [2] in annex B) to be 100,3 % using flame atomic absorption spectrometry; and the mean analytical recovery for spiked filters in the range 0,01 µg to 0,6 µg of cadmium was determined (see reference [2] in annex B) to be 97,9 % using electrothermal atomic absorption spectrometry.

NOTE 42 If the wet-ashing procedure specified in 8.2.2 is ineffective for the digestion of particulate cadmium compounds present in the test atmosphere, and an alternative more vigorous digestion procedure has not been used (see 10.1), results will be subject to a significant negative bias.

9.2.2 In laboratory experiments, the component of the coefficient of variation of the method that arises from analytical variability, $\text{CV}_{\text{analysis}}$, has been determined (see reference [2] in annex B) to be less than 10 % for samples in the range 0,15 µg to 1 µg and less than 3 % for samples in the range 1 µg to 96 µg using flame atomic absorption spectrometry; and less than 5 % for samples in the range 0,01 µg to 0,6 µg using electrothermal atomic absorption spectrometry. This gives a measure of the repeatability of the analytical method.

NOTE 43 The repeatability of an atomic absorption method at a given level is defined in ISO 6955:1982, subclause 6.2.7 as the closeness of agreement between successive results obtained using the same method on identical material submitted for the test under the same conditions (same operator, same equipment, same set of reagents, same laboratory).

9.2.3 The overall uncertainty of the method (see note 44), as defined in EN 482, has been determined (see reference [2] in annex B) to be less than 25 % for samples in the range 0,15 µg to 1 µg and less than 15 % for samples in the range 1 µg to 96 µg using flame atomic absorption spectrometry; and less than 17 % for samples in the range 0,01 µg to 0,6 µg using electrothermal atomic absorption spectrometry.

This assumes that the coefficient of variation of the method that arises from inter-specimen sampler variability, CV_{inter}, is negligible and that the coefficient of variation of the method that arises from flow-rate variability, CV_{flow}, is limited to 5 % (see 7.3.4).

These figures are within the specifications prescribed in EN 482 for overall uncertainty of measurements for comparison with limit values (see note 45).

NOTES

44 Overall uncertainty (of a measuring procedure or of an instrument) has been defined in EN 482 (reference [5] in annex B) as the quantity used to characterize as a whole the uncertainty of a result given by an apparatus or measuring procedure. It is expressed, on a relative basis, by a combination of bias and precision, usually according to the formula

$$\frac{|\bar{x} - x_{\text{ref}}| + 2s}{x_{\text{ref}}} \times 100$$

where

$\bar{x}$ is the mean value of results of a number n of repeated measurements;

x_{ref} is the true or accepted reference value of concentration;

s is the standard deviation of measurements.

45 CEN (see EN 482) has described general performance requirements for the performance of procedures for the measurement of chemical agents in workplace atmospheres. Upper limits of acceptability for relative overall uncertainty have been specified for a number of measurement tasks, and these may be used as a guide for the purposes of this International Standard. CEN requirements are less stringent for screening measurements than for measurements for comparison with limit values; and they are less stringent for measurements for comparison with limit values when these are made in the range 0,1 to 0,5 times the exposure limit value (overall uncertainty less than 50 %) than when they are made in the range 0,5 to 2,0 times the exposure limit value (overall uncertainty less than 30 %).

9.2.4 A sampling efficiency of 1,00 has been determined (see reference [3] in annex B) for the filter collection step for laboratory-generated cadmium oxide aerosols.

9.3 Detection limit and working range

9.3.1 The qualitative and quantitative instrumental detection limits for cadmium defined as three times and ten times the standard deviation of absorbance measurements made as described in 8.5, have been estimated (see reference [2] in annex B) to be 0,003 6 µg/ml and 0,012 µg/ml for flame atomic absorption spectrometry; and 0,071 ng/ml and 0,24 ng/ml for electrothermal atomic absorption spectrometry. For an air sample volume of 30 litres and a sample solution volume of 10 ml, this corresponds to cadmium-in-air concentrations of 1,2 µg/m^3 and 4 µg/m^3 for flame atomic absorption sectrometry; and 0,024 µg/m^3 and 0,08 µg/m^3 for electrothermal atomic absorption spectrometry.

9.3.2 The working range of the method is approximately 0,002 5 µg to 0,025 µg of cadmium per sample for electrothermal absorption spectrometry and 0,125 µg to 10 µg of cadmium per sample for flame atomic absorption spectrometry using the normal procedure, without dilution.

10 Special cases

10.1 If there is any doubt about the suitability of the wet-ashing procedure specified in 8.2.2 for digestion of particulate cadmium compounds which may be present in the test atmosphere, determine its effectiveness by analysing a bulk sample of known cadmium content, which is representative of the material in the test atmosphere. If the efficiency of recovery is less than 95 %, use an alternative, more vigorous digestion procedure which is not specified in this International Standard. Do not use a correction factor to compensate for an apparently ineffective digestion procedure, since this may also lead to erroneous results.

NOTE 46 In designing an experiment to determine the effectiveness of the wet-ashing procedure, it should be recognized that the particle size distribution of a bulk sample may have an important influence on the efficiency of its dissolution. Also, amounts in micrograms of relatively insoluble material are frequently much more readily soluble than bulk amounts.

10.2 Only silicon has been found to exhibit any chemical interference in the atomic absorption determination of cadmium (see reference [4] in annex B), and this is not solubilized by the wet-ashing procedure specified in 8.2.2.

10.3 The 228,8 nm cadmium line is subject to possible spectral interference from arsenic (see reference [4] in annex B).

11 Test report

The test report shall include the following information:

a) all details necessary for a complete identification of the air sample, including the date of sampling, the place of sampling, the type of sample (personal or fixed location), and either the identity of the individual whose breathing zone was sampled (for a personal sample) or the location at which the general occupational environment was sampled (for a fixed-location sample);

b) a reference to this International Standard and to the atomic absorption spectrometric method used (flame or electrothermal);

c) the type and diameter of filter used;

d) the type of sampler used;

e) the type of sampling pump used, and its identification;

f) the type of flowmeter used, the primary standard against which it was calibrated, the range of flow rates for which the flowmeter was calibrated, and the atmospheric temperature and pressure at which it was calibrated, if appropriate (see 7.1.3.2);

g) the time at the start and end of the sampling period, and the duration of the sampling period, in minutes;

h) the flow rate at the start and end of the sampling period, and the mean flow rate, in litres per minute;

i) the mean atmospheric temperature and pressure during sampling, if appropriate (see 7.1.3.1);

j) the volume of air sampled, in litres, at ambient conditions;

k) the name of the person who collected the sample;

l) the mass concentration of cadmium in the air sample, in milligrams per cubic metre, at ambient conditions and, if appropriate (see 7.1.3.1), adjusted, as required for compliance with national standards and regulations, to reference conditions, e.g. 20 °C or 25 °C;

m) the analytical variables used in 9.1 to calculate the mass concentration of cadmium in the air sample, including the cadmium concentration in the sample solution and blank test solution, the volume of the sample solution and blank test solution, and the dilution factor;

n) any interferents known to be present;

o) the estimated detection limit under the working analytical conditions (see 8.5.3);

p) any operation not specified in this International Standard, or regarded as optional;

q) the name of the analyst;

r) the date of the analysis.

Annex A
(informative)

Typical operating parameters for determination of cadmium by electrothermal atomic absorption spectrometry

Mode:	Peak area
Integration time:	5 s
Background correction:	Zeeman
Injection volumes:	20 µl of reference or sample solution and 10 µl of matrix-modifier solution

Table A.1 — Typical temperature profile for determination of cadmium by electrothermal atomic absorption spectrometry

Step	Ramp time s	Hold time s	Furnace temperature °C	Argon flow ml/min	Read
1 Dry	40	30	120	300	
2 Ash	10	20	850	300	
3 Cool down	1	15	20	300	
4 Atomize	0	5	1 650	0	*
5 Clean	1	5	2 600	300	

Table A.2 — Typical autosampler injection volumes for the *in situ* preparation of matrix-modified reference and sample solutions

Matrix-modified solution¹⁾	Volume of working reference solution µl	Volume of working reference blank solution µl	Volume of matrix-modified solution µl	Volume of sample solution µl
0 ng/ml reference solution	—	20	10	—
0,5 ng/ml reference solution	4	16	10	—
1,0 ng/ml reference solution	8	12	10	—
1,5 ng/ml reference solution	12	8	10	—
2,0 ng/ml reference solution	16	4	10	—
2,5 ng/ml reference solution	20	—	10	—
Sample solution	—	—	10	20
Sample solution dilution	—	$20 - x$	10	x

1) The cadmium concentrations in the matrix-modified reference solutions are notional, in that they relate to the 20 µl sample solution volume, i.e. the 10 µl volume of matrix-modifier solution is ignored.