INTERNATIONAL STANDARD

ISO 7086-1

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Glass hollowware in contact with food — Release of lead and cadmium —

Part 1:
Test method

Vaisselle creuse en verre en contact avec les aliments — Émission de plomb et de cadmium —

Partie 1: Méthode d'essai

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Foreword

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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).

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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 166, *Ceramic ware, glassware and glass ceramic ware in contact with food*.

This third edition cancels and replaces the second edition (ISO 7086-1:2000), which has been technically revised. The main changes to the previous edition are as follows:

- technical procedures have been updated;
- permissible limits for metal release have been brought in line with current regulatory limits in major markets and in harmony with as many regional or national standards as is practical.

A list of all parts in the ISO 7086 series can be found on the ISO website.

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.

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Introduction

Release of potentially toxic metals, particularly lead and cadmium, from glassware surfaces is an issue which requires effective means of control to ensure the protection of the population against possible hazards arising from the use of improperly formulated and/or processed glass hollowware used for the preparation, serving and storage of food and beverages.

As a secondary consideration, different requirements from country to country for the control of the release of toxic metals from the surfaces of glassware present non-tariff barriers to international trade in these commodities. Accordingly, there is a need to maintain internationally accepted methods of testing glassware for potentially toxic metal release.

The revision of this document was necessary to take into consideration recent developments in the application of the analytical technique inductively coupled plasma mass spectrometry (ICP-MS).

The test method is a combination of a leach procedure, which is the core of the document, and of the analytical method.

ICP-MS is the reference analytical method as it is generally considered as the most accurate analytical method, although other methods have their own merits. Flame atomic absorption is kept as an alternative method. Other validated analytical methods, such as graphite furnace atomic absorption spectrometry (GFAAS) or inductively coupled optical emission spectrometry (ICP-OES), may also be used, considering the appropriate accuracy to the level of release of lead and cadmium to be measured.

The limits in ISO 7086-2 are set on the basis of a single extraction into the extraction solution. ISO 7086-2:2000, 8.5 specifies that all repeat-use articles are tested three times with fresh extraction solution and the results of the third test reported for conformity with the permissible limits. It has been demonstrated that metal release into the third extraction is always less than the release into the first extraction. Therefore, data from a third extraction will show false conformity with the limits specified in ISO 7086-2. New limits that are appropriate to third extraction data are currently being agreed.

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Glass hollowware in contact with food — Release of lead and cadmium —

Part 1:
Test method

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WARNING — The use of this document may involve hazardous materials, operations and equipment. This document does not purport to address all the risks associated with its use. It is the responsibility of the user of this document to establish appropriate safety and health practices and determine the applicability of national regulatory limitations prior to use.

IMPORTANT — It is absolutely essential that tests, conducted in accordance with this document, be carried out by suitably qualified staff.

1 Scope

This document specifies a test method for the release of lead and cadmium from glass hollowware that is intended to be used in contact with food.

This document is applicable to glass hollowware intended for use in the preparation, cooking, serving and storage of food and beverages, excluding glass ceramic ware and glass flatware.

This document is also applicable to glass articles used for packaging in the food industry.

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 385, *Laboratory glassware — Burettes*

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*

3 Terms and definitions

For the purposes of this document, the following terms and definitions 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 http://www.electropedia.org/

3.1
atomic absorption
absorption of electromagnetic radiation by free atoms in the gas phase wherein a line spectrum is obtained which is specific for the absorbing atoms

3.2
atomic absorption spectrometry
AAS
spectroanalytical method for qualitative determination and quantitative evaluation of element concentrations wherein the technique determines these concentrations by measuring the *atomic absorption* (3.1) of free atoms

3.3
flame atomic absorption spectrometry
FAAS
atomic absorption spectrometry (3.2) that uses a flame to create free atoms of the analyte in the gas phase

3.4
graphite furnace atomic absorption spectrometry
GFAAS
atomic absorption spectrometry (3.2) involving electrothermal atomization in a graphite furnace

3.5
inductively coupled plasma mass spectrometry
ICP-MS
analytical method for qualitative determination and quantitative evaluation of element concentrations by measuring the ions produced by a radiofrequency inductively coupled plasma

Note 1 to entry: In the mass spectrometer the ions are separated and the elements identified according to their mass-to-charge ratio m/z, while the concentration of the elements is proportional to the numbers of ions.

3.6
inductively coupled optical emission spectrometry
ICP-OES
trace-level, elemental analysis technique that uses the emission spectra of a sample to identify and quantify the elements present

3.7
extraction solution
4 % per volume acetic acid solution recovered after the extraction test and which is analysed for lead and cadmium concentration

3.8
surface area
area that is intended to come into contact with foodstuffs in normal use

3.9
drinking rim
20 mm-wide section of the external surface of the vessel, measured downwards from the upper edge along the wall of the vessel

3.10
test solution
4 % per volume acetic acid solution used in the test to extract lead and cadmium from the article

3.11
foodware
articles which are intended to be used for the preparation, cooking, serving and storage of food or drinks

3.12
glassware
articles which are intended to be used in contact with foodstuff and made of glass

Note 1 to entry: Glass is an inorganic material produced by the complete fusion of raw materials at high temperature into a homogeneous liquid which is then cooled to a rigid condition, essentially without crystallization.

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Note 2 to entry: The material may be clear, coloured or opaque, depending on the level of colouring and opacifying agents used.

3.13
flatware
glassware (3.12) that has an internal depth not exceeding 25 mm, measured from the lowest point to the horizontal plane passing through the point of overflow

3.14
glass hollowware
glassware (3.12) that has an internal depth greater than 25 mm, measured from the lowest point to the horizontal plane passing through the point of overflow

Note 1 to entry: glass hollowware is subdivided into three categories based on volume:

- small: hollowware with a capacity of less than 600 ml;
- large: hollowware with a capacity of between 600 ml and 3 l;
- storage: hollowware with a capacity of 3 l or greater.

3.15
glass ceramic ware
articles which are intended to be used in contact with foodstuffs and made of glass ceramic

Note 1 to entry: Glass ceramic is an inorganic material produced by the complete fusion of raw materials at high temperatures into a homogeneous liquid which is then cooled to a rigid condition and temperature treated in such a way as to produce a mostly microcrystalline body.

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4 Principles

Glassware and other silicate surfaces are placed in contact with test solution (5.1.3) for (24 ± 0,5) h at (22 ± 2) °C to extract lead and/or cadmium, if present, from the surfaces of the articles or test specimens.

The amounts of extracted lead and cadmium are determined by an adequate analytical method. Inductively coupled plasma mass spectrometry (ICP-MS) is the reference analytical method as it is generally considered as the most accurate analytical method, although other methods have their own merits. Flame atomic absorption spectrometry (FAAS) is kept as an alternative. Both methodologies are described in detail in Annexes A and B.

Other validated analytical methods, such as graphite furnace atomic absorption spectrometry (GFAAS) or inductively coupled optical emission spectrometry (ICP-OES), may also be used considering the appropriate accuracy to the level of release of Pb and Cd to be measured. In the case of ICP-OES, it is recommended that the methodology described in Annex C is applied.

For certain specific articles and applications as defined in ISO 7086-2, the (24 ± 0,5) h duration is replaced by (2 ± 0,1) h using the same test solution and temperature.

5 Reagents and materials

5.1 Reagents

All reagents shall be of recognized analytical grade.

For the determination of lead and cadmium at traces and ultra traces level, the reagents shall be of adequate purity. The concentration of the analyte or interfering substances in the reagents and the water should be negligible compared with the lowest concentration determined.

5.1.1 **Water** grade 1, as specified in ISO 3696, for all sample preparations and dilutions.

5.1.2 Acetic acid, (CH3COOH), glacial, ρ = 1,05 g/ml.

5.1.3 Acetic acid test solution, with a volume fraction of 4 %.

Add 40 ml of acetic acid (5.1.2) to water (5.1.1) with a one-mark pipette (6.2.4) and dilute to 1 l in a one-mark volumetric flask (6.2.5). This solution shall be freshly prepared for use. Proportionately greater quantities may be prepared.

5.2 Materials and supplies

5.2.1 Paraffin wax with a melting point in the range 56 °C to 58 °C.

5.2.2 Washing agent, commercially available non-acidic manual dishwashing detergent in dilution recommended by a manufacturer.

5.2.3 Silicone sealant, capable of forming a ribbon of sealant approximately 6 mm in diameter.

This sealant shall not leach acetic acid, cadmium or lead to the test solution.

6 Apparatus

6.1 Analytical techniques

ICP-MS, FAAS and inductively coupled plasma optic emission spectrometry (ICP-OES) are described in Annexes A, B and C, respectively.

GFAAS is also a permitted option.

6.2 Accessories

6.2.1 Assorted laboratory ware, as required, made of borosilicate glass as specified in ISO 3585.

6.2.2 Burette, of capacity 25 ml, graduated in divisions of 0,05 ml, conforming with ISO 385 class B or better.

6.2.3 Covers for the articles under test, for example plates, watch-glasses or Petri dishes of various sizes. Covers shall be opaque if a darkroom is not available.

6.2.4 One-mark pipettes, of capacities 10 ml and 100 ml, conforming with ISO 648, class B or better. Other sizes as required.

6.2.5 One-mark volumetric flasks, of capacities 100 ml and 1 000 ml, conforming with ISO 1042, class B or better. Other sizes as required.

6.2.6 Precision piston pipettes, typically 1 000 µl and 500 µl.

6.2.7 Straight edge and depth gauge, calibrated in millimetres.

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7 Sampling

7.1 Priority

When selecting samples from a mixed lot of foodware, articles that have the highest surface area/volume ratio should be prioritized.

7.2 Sample size

At least four items shall be measured. Each of the articles shall be identical in size, shape, colour and decoration.

7.3 Preparation and preservation of test samples

Samples of ware shall be clean and free from grease or other matter likely to affect the test. Briefly wash the specimens in an aqueous solution at (40 ± 5) °C at hand-hot temperature using tap water containing 1 ml/l of a non-acidic domestic detergent. Rinse in tap water and then in water (5.1.1). Drain and dry either at a temperature of (40 ± 5) °C in a drying oven or by wiping with a new piece of filter paper. Do not use any sample that shows residual staining. Do not handle the surfaces to be tested after cleaning.

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8 Procedures

8.1 Extraction

8.1.1 Extraction temperature

Conduct the extraction at a temperature of (22 ± 2) °C in the dark.

8.1.2 Leaching

Fill each specimen with test solution to 1 mm from overflowing, as measured vertically. Cover the specimen. Leach for (24 ± 0,5) h, or (2 ± 0,1) h depending on the case studied.

8.1.3 Sampling of the extraction solution for analysis

Prior to sampling, mix the extraction solution by stirring or another appropriate method that avoids loss of the extraction solution or abrasion of the surface. Remove the amount of the extraction solution required by the considered analytical method with a pipette and transfer it to a suitable storage container.

Analyse the extraction solution as soon as possible since there is a risk of adsorption of lead or cadmium on to the walls of the storage container, particularly when Pb and Cd are present in low concentrations.

8.1.4 Drinking rim

The drinking rims of glass hollowware shall be tested by marking each of four units (20 ± 1) mm below the rim on the outside. Each item is placed inverted in a suitable laboratory glassware container with a diameter between 1,25 and 2 times that of the item. Add sufficient test solution (5.1.3) to the glassware container to fill to the 20 mm mark on the item. Leave to stand for (24 ± 0,5) h, or (2 ± 0,1) h depending on the considered case, at (22 ± 2) °C (in the dark for cadmium determinations) and protect from excessive evaporation. Carefully cover the portion of the external surface of the article that is not to be tested with melted paraffin wax. Cover any handle present in the drinking rim region to be tested in the same way.

Before sampling the leachate, add test solution (5.1.3) to the glass container as necessary in order to re-establish the (20 ± 1) mm level.

It is permissible for the drinking rim to be cut off and tested separately.

Determine lead and cadmium by the appropriate analytical methodology and report the results.

8.2 Articles used in repeated contact with foodstuffs or beverages

When an article is intended to come into repeated contact with foodstuffs or beverages, the release tests are carried out three times on the same test sample, using a fresh sample of the test solution (5.1.3) on each occasion. If the level of release conforms with the first migration, further testing is not necessary.

According to the specific category of article defined in ISO 7086-2, the conformity of the material is then checked on the basis of the concentration in the extraction solution in the third test.

Wash the article between each contact with water (5.1.1).

9 Analytical methods

9.1 General

Three analytical methods using ICP-MS, FAAS or ICP-OES are described in Annexes A, B and C, respectively.

GFAAS is also a permitted option.

9.2 Calculation of release of lead and cadmium from hollowware

The lead or cadmium released is obtained directly by the lead or cadmium concentrations of the sample extraction solution and expressed in micrograms per litre.

9.3 Calculation of release of lead and cadmium from drinking rim

The release of lead and cadmium per article from the drinking rim shall be calculated by multiplying the lead or cadmium concentrations by the volume of the test solution. This value shall be expressed in micrograms per article.

Another option is to calculate the release of lead and cadmium from the drinking rim per unit of surface by multiplying the lead or cadmium concentrations by the volume of the test solution, and dividing by the rim area. In this case, the value shall be expressed in micrograms per square decimetre.

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10 Test report

The test report shall include the following information:

a) reference to this document, i.e. ISO 7086-1, including the year of publication;

b) identification of the sample, including type and origin where available;

c) the reference to the calculation used, as listed in Clause 9, with the following information, when appropriate: the surface area, the filling volume and the surface of the rim area for drinking rim testing;

d) the number of samples tested (minimum four samples);

e) the analytical method used, with the information required for the settings according to Annexes A to C;

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f) the test results, expressed as individual values for each specimen and the mean value for test sample groups;

g) the date of the extraction test and the analytical tests;

h) any unusual features observed.

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Annex A
(informative)

Analytical method using ICP–MS

A.1 General

This annex describes a method for the determination of lead and cadmium in extraction solutions by ICP-MS.

A.2 Principles

Determination of lead and cadmium by ICP-MS consists of the following steps:

1) introduction of a measuring solution into a radiofrequency plasma to cause dissolution, atomization and ionization of elements;
2) extraction of the ions from plasma through a differentially pumped vacuum interface and separation on the basis of their mass-to-charge ratio by a mass spectrometer;
3) transmission of the ions through the mass separation unit and detection, usually by a continuous dynode electron multiplier assembly, and ion information processing by a data-handling system;
4) quantitative determination after calibration with suitable calibration solutions.

The relationship between signal intensity and mass concentration is usually a linear one over at least five orders of magnitude. For more details refer to ISO 17294-1.

A.3 Interferences

It is important to underline that when using ICP-MS, the presence of concomitant elements in the sample can cause interferences, for instance systematic errors in the measurement of the signal. Interferences are classified into spectral and non-spectral interferences.

The components that can cause spectral interferences are:

1) An isotope of another element that has the same nominal mass-to charge-ratio as the analyte isotope, for example ^{114}Cd (analyte) and ^{114}Sn (interferant). Isobaric interferences may be corrected using the aboundance of a different isotope of the interfering element (Table A.1). However, correction options are often included in the instrument software. The isotope for measurements can usually be chosen free from isobaric interferences.
2) Polyatomic or molecular and doubly charged ion interferences. In many cases these ions contain argon (plasma gas) and/or oxygen originating from the water of the solution aspirated, for example $^{114}MoO^+$ (interferant) and ^{111}Cd, ^{114}Cd (analyte). Significant molecular and doubly charged interferences shall be corrected for.

EXAMPLE Corrected cadmium signal (using natural isotopes abundances for coefficient approximations): ^{114}Cd = (m/z 114 signal) − (0,026 84)(^{118}Sn signal).

Non spectral physical interferences are associated with the sample nebulisation and transport processes as well as with ion-transmission efficiencies. Nebulisation and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enchantement. Dissolved solids can deposit on the nebuliser tip of a pneumatic nebuliser and on the interface skimmers. Total solid levels below

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0,2 % (2 000 mg/l) are recommended to minimize solid deposition. An internal standard can be used to correct for physical interferences if it is carefully matched to the measurement element so that the two elements are similarly affected by matrix changes. Dilution of the sample fivefold will usually eliminate the problem.

The following correction formula shall be applied:

(1 000) (206Pb) + (1 000) (207Pb) + (1 000) (208Pb)

Detailed information on spectral and non-spectral interferences is given in ISO 17294-1:2004, 6.1.

Table A.1 — Lead and cadmium spectral interferences

Element	**Isotope**	**Abundance** %	**Theoretical interferences**		**Interference with practical relevance**
			Inter-element	**Polyatomic ions**	
Cd	111	**12,8**	—	MoO, MoOH, ZrOH,-K$_2$O$_2$H	^{94}Zr^{16}O^{1}H ^{95}Mo^{16}O
	113	**12,2**	**In**	MoO, ZrOH, Ca$_2$O$_2$H, Ar$_2$O$_2$H, RuO	In, ^{97}Mo^{16}O
	114	**28,7**	**Sn**	MoO, MoOH, RuO	Sn, ^{98}Mo^{16}O
Pb[a]	206	**24,1**	—	PtO	—
	207	**22,1**	—	IrO	—
	208	**52,4**	—	PtO	—

[a] All three isotopes shall be used to quantify lead to allow for the variability of lead isotopes in nature.

A.4 Reagents

All reagents shall be of recognized analytical grade. For the determination of elements at traces and ultratrace level, the reagents shall be of adequate purity. The concentration of the analyte or interfering substances in the reagents and the water should be negligible compared with the lowest concentration to be determined.

Nitric acid should be used to minimize interference by polyatoms.

A.4.1 Water, grade 1 as specified in ISO 3696 for all sample preparations and dilutions.

A.4.2 Acetic acid, (CH_3COOH), glacial, ρ = 1,05 g/ml.

A.4.3 Acetic acid test solution, with a volume fraction of 4 %.

Add 40 ml of acetic acid (A.4.2) to water (A.4.1) with a one-mark pipette (6.2.4), and fill to 1 l in a one-mark volumetric flask (6.2.5). This solution shall be freshly prepared for use. Proportionately greater quantities may be prepared.

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A.4.4 Nitric acid, r(HNO3) = 1,4 g/ml.

Nitric acid is available both as:

r(HNO3) = 1,40 g/ml equivalent to w(HNO3) = 650 g/kg

or

r(HNO3) = 1,42 g/ml equivalent to w(HNO3) = 690 g/kg

Both are suitable for use in this method.

A.4.5 Elements stock solution (lead, cadmium, internal standards).

Single-element stock solutions and multi-element stock solutions with adequate specification stating the acid used and the preparation technique are commercially available. For example, element stock solutions with concentrations of the analytes of 1 000 mg/l are suitable. These solutions are considered to be stable for more than one year, but in reference to guaranteed stability, the recommendations of the manufacturer should be considered.

A.4.6 Lead and cadmium standard solutions: ρ (Pb) = 10 mg/l – ρ (Cd) = 10 mg/l.

Pipette, with a one-mark pipette (6.2.4), 10 ml of Pb and Cd element stock solutions of 1 000 mg/l separately or together, if suitable, into a 1 000 ml one-mark volumetric flask (6.2.5.). Add 10 ml of nitric acid. Bring to volume with water and transfer to a suitable storage bottle.

A.4.7 Lead and cadmium intermediate standard solutions: ρ (Pb) = 1 mg/l – ρ (Cd) = 1 mg/l.

Pipette, with a one-mark pipette (6.2.4), 10 ml of Pb and Cd element stock solutions of 10 mg/l separately or together, if suitable, into a 100 ml one-mark volumetric flask (6.2.5). Bring to volume with water and transfer to a suitable bottle. Prepare the intermediate standard solutions freshly before each use.

A.4.8 Internal standard solution (reference element solution).

The choice of elements for the reference-element solution depends on the analytical problem. Solutions of these elements should cover the mass range of interest. Generally, an internal standard should be no more than 50 amu removed from the analyte. The concentrations of these elements in the sample should be negligibly low.

The elements ^{85}Y, ^{103}Rh, ^{165}Ho and ^{187}Re, for example, could be suitable for this purpose.

The following internal standard solutions may be used: ρ (Y, Rh, Ho and Re) = 5 mg/l.

Pipette, with a one-mark pipette (6.2.4), 5 ml of each element stock solution (1 000 mg/l of each Y, Rh, Ho and Re) into a 1 000 ml one-mark volumetric flask (6.2.5). Add 10 ml of nitric acid. Bring to volume with water and transfer to a suitable storage bottle.

A suitable concentration range of the internal standard in samples and calibration solutions is 10 µg/l to 100 µg/l.

A.4.9 Lead and cadmium calibration solutions.

A calibration solution is a solution used to calibrate the instrument, prepared from stock solutions or from a certified standard.

Prepare the calibration solution(s) that cover the required working range by diluting the element standard solutions or intermediate element standard solutions.

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Add an adequate volume of test solution (A.4.3) to make the composition of the calibration solutions equal to the composition of the test sample solutions to minimize the matrix effect. If necessary, add internal standard solution to a concentration of, for example, 10 µg/l or 100 µg/l of the reference elements before bringing up to volume.

A.4.10 Calibration blank solution.

The calibration blank solution is prepared in the same way as the calibration solutions but the analytes are left out. Prepare the calibration blank solution by adding an adequate volume of test solution (A.4.3) to make the composition of the calibration blank solutions equal to the composition of the test sample. If necessary, add internal standard solution to a concentration of, for example, 10 µg/l or 100 µg/l of the reference elements before bringing up to volume.

A.4.11 Initial calibration verification solution.

The calibration verification solution is prepared by combining lead and cadmium from a standard source different from that of the calibration standard, and at concentration near the midpoint of the calibration curve. This standard may also be purchased. The solution should be prepared in the same acid composition (matrix) of the calibrations and the test samples.

A.4.12 Continuing calibration verification solution.

The continuing calibration verification standard solution should be prepared combining lead and cadmium from the same standards used for calibration, at a concentration near the mid-point of the calibration curve. The solution should be prepared in the same acid composition (matrix) of the calibrations and the test samples.

A.4.13 Interference check solution.

The interference check solution (ICS) is prepared to contain known concentrations of interfering elements (Table A.1) that will demonstrate the magnitude of interferences and provide an adequate test of any corrections, for example Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various molecular-ion isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits. These solutions shall be prepared from ultrapure reagents or they can be obtained commercially.

A.4.14 Optimization solution or tune solution.

The optimization solution, or tune solution, commercially available, serves for mass calibration and for optimization of the ICP-MS apparatus conditions, for example adjustment of maximal sensitivity with respect to minimal oxide formation rate and minimal formation of doubly charged ions. It should contain elements covering the entire mass range, as well as elements prone to a high oxide formation rate or to the formation of doubly charged ions.

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A.5 Apparatus

A.5.1 Inductively coupled plasma mass spectrometer

ICP-MS system includes:

- sample introduction system (pump, nebuliser, spray chamber);
- inductively coupled plasma (radio-frequency generator, load coil, torch);
- quadrupole or time-of-flight mass spectrometer, capable of scanning a mass range suitable with an appropriate resolution;

- suitable equipment for polyatomic interference attenuation, typically a collision cell;
- process control and data processing equipment;
- argon gas supply – high purity grade, i.e. > 99,99 %;
- helium for collision cell – ultra-high purity grade, i.e. > 99,999 %;
- optional autosampler or additional (peristaltic) pump.

For more detailed information on the instrumentation, refer to ISO 17294-1.

A.5.2 Accessories

The stability of test samples and calibration solutions depends to a high degree on the container material. The material shall be checked according to the specific purpose. For the determination of lead and cadmium in 4 % per volume acetic acid solutions, high-density polyethene (HDPE) or polytetrafluoroethene (PTFE) containers (e.g. falcon tubes and storage bottles) are allowed.

Immediately before use, all laboratory ware used to prepare stock and standard solutions should be washed thoroughly with warm diluted nitric acid, for example $w(HNO_3) = 10$ %, and then rinsed several times with water (A.4.1).

The use of piston pipettes is permitted and also enables the preparation of lower volumes of calibration solutions. The application of dilutors is also allowed.

For more detailed information on the instrumentation, refer to ISO 17294-1.

A.6 Procedures

A.6.1 Instrument setup

Adjust the instrumental parameters of the ICP-MS system in accordance with the manufacturer's manual.

Wait at least 30 min to stabilize the plasma and adjust the instrument to working condition.

For guidance consult ISO 17294-1.

For the selection of suitable isotopes (ISO 17294-1:2004, Table 1), use the recommended optimization solution to optimize or check the sensitivity and the stability of the system. Check the resolution and the mass calibration as often as required by the manufacturer. Define the relative atomic masses and the corresponding corrections. Define take-up and rinsing times to avoid memory effects.

Either standard mode or spectrum helium mode (kinetic energy discrimination) are acceptable.

The use of an internal standard is recommended. Add the internal standard solution to the interference check solution to calibration solutions, to the blank calibration solutions and to all test portions of samples before the analysis or add the internal standard solution online using a two-channel sample-introduction pump. The mass concentration of the reference elements shall be the same in all solutions.

A.6.2 Calibration

Before calibration, it is important to aspirate the blank solution for 10 min to stabilize the plasma.

When the analytical system is first evaluated, establish a calibration curve for lead and cadmium using at least five measuring points (for example, the blank calibration solution and four calibration solutions over a linear range). The calibration range should encompass the Pb/Cd concentrations of the sample.

The working range should be above the limit of quantification (LOQ) and is frequently within the range of 0,2 µg/l to 200 µg/l or a part of this.

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For work on a daily basis, one blank solution and one to two calibration solutions are enough to set up a calibration graph, but check the validity of the calibration curve with a certified reference sample, a standard sample or a suitable internal control sample.

For more details refer to ISO 17294-1:2004, 9.2.

Linear regression correlation coefficient (r) shall be ≥ 0,998.

If correlation coefficient is < 0,998, repeat calibration.

A.6.3 Determination of lead and cadmium

After establishing the calibration curves, measure the blanks and the interference check solution to establish interference correction or to check presence of interferences.

Run the test samples and if the lead and cadmium concentration of the extraction solutions are found to be higher than the highest calibration point, dilute a suitable aliquot portion to reduce concentrations within the working range with test solution (3.10) and water (A.4.1) in order to have the same acidity composition as the calibration curve.

Within sufficient small intervals (for example, every 25 samples or less and at the beginning and end of the sample run) check the accuracy of at least one certified reference sample, one standard sample or a suitable internal control sample. If necessary, recalibrate.

The limit of detection (LOD) is the minimum value of the measurand for which the measuring system is not in the basic state, with a stated probability. The LOD, also referred to as capability of detection, is defined by reference to the applicable basic state. The measurement value can be distinguished from the analytical blank value with a confidence of 99 %. The LOD is expressed as the mean analytical blank value (b_{ave}) plus three times the standard deviation of the analytical blank (s_{b}), as shown in Formula (A.1).

$$L_{\mathrm{D}} = b_{\mathrm{ave}} + 3s_{\mathrm{b}} \tag{A.1}$$

where

L_{D} is the limit of detection;

b_{ave} is the mean analytical blank value: a value determined by a blank sample covering the complete analytical procedure including extraction, clean-up, identification and quantification, including all the relevant reagents and materials.

s_{b} is the standard deviation of the analytical blank.

The LOD should preferably be calculated from the analytical blank b_{ave}. If this is not possible, the LOD can be calculated from the signal-to-noise ratio.

The LOQ is the limit above which a quantification of the measurand is possible, expressed as the mean analytical blank value plus six times the standard deviation of the analytical blank. The factor F depends on the accepted measurement uncertainty [see Formula (A.2)].

$$L_{\mathrm{Q}} = b_{\mathrm{ave}} + Fs_{\mathrm{b}} \tag{A.2}$$

where

L_{Q} is the limit of quantification;

b_{ave} is the mean analytical blank value;

s_{b} is the standard deviation of the analytical blank.

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The LOQ should preferably be calculated from the analytical blank b_{ave}. If this is not possible, the LOQ can be calculated from the signal-to-noise ratio.

A.7 Calculations

The mass concentrations for each element are determined with the aid of the instrument software. Carry out the following single steps for each element.

a) Correct the count rates according to the respective equations.

b) Make allowance for the count rates from the blank calibration and calibration solutions, and relate to the count rates of the internal standard solution. Determine the slope and the intercept on the ordinate.

c) Determine the mass concentrations of samples with the aid of the count rates and the calibration graphs.

According to the requirements set by the analytical quality control, the determination of the mass concentrations using the software of the apparatus shall be verifiable and shall be documented. In all cases, it shall be clear which corrections have been carried out with the aid of the software.

A.8 Expression of results

State as many significant figures as are acceptable according to the precision of the measuring values, but not more than three significant figures.

A.9 Quality control

A.9.1 Instrument detection limit (L_{DI})

Smallest concentration that can be detected with a defined statistical probability using a contaminant-free instrument and blank calibration solution.

A.9.2 Blank

Result of the calibration blank check shall be within three times the instrumental detection limit.

A.9.3 Calibration verification and drift

Result of the initial and continuing calibration verification solutions shall not deviate by more than 10 %.

A.9.4 Internal standard abundance

Internal standard shall not deviate by more than 20 %.

A.9.5 Interference

The impact on the measured value of uncorrected isobaric, molecular and doubly charged interferences shall not be higher than 5 % or three times the instrumental detection limit.

Successive values of a correction factor shall not differ by more than 20 %.

A.10 Precision

An interlaboratory trial, carried out among European reference and official control laboratories for food contact materials in 2014, yielded the results given in Table A.2. The sample used in the interlaboratory trial was a 4 % per volume acetic acid solution spiked with the elements reported in Table A.3.

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Table A.2 — Precision data for the determination of lead and cadmium in 4 % per volume acetic acid solution using ICP-MS

Element	*l*	*n*	$\bar{x}$	σ_R	**Reproducibility CV**	σ_r	**Repeatability CV**
			µg/l	µg/l	**%**	µg/l	**%**
Pb	30	114	9,58	0,99	10,32	0,20	2,13
Cd	29	111	4,89	0,24	4,89	0,09	1,77

Key

l: Number of laboratories

n: Number of values

$\bar{x}$: Robust mean

σ_R: Reproducibility standard deviation

CV: Coefficient of variation

σ_r: Repeatability standard deviation

Lead and cadmium were measured in 4 % per volume acetic acid solutions.

All precision criteria were derived applying robust statics without elimination of outliers (ISO 5725-5).

Table A.3 — Sample used for the interlaboratory trial

Sample matrix	**Spiked element**	**Concentration** µg/l[a]
4 % per volume acetic acid solutions	Pb	**9,44**
	Cd	**4,89**
	Ba	787
	Co	**51,4**
	Mn	401
	Ni	**70,8**
	As	**13,0**
	Al	727

[a] Robust mean from participants' results.

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Annex B
(informative)

Analytical method using FAAS

B.1 General

This annex describes an analytical method by FAAS for the determination of lead and cadmium in extraction solution.

B.2 Principles

Determination of lead and cadmium by FAAS consists of the following steps:

1) introduction of a measuring solution into the FAAS;

2) measurement of the absorption;

3) quantitative determination of the Pb and Cd after calibration with suitable calibration solutions.

Bracketing technique: analytical method consisting of bracketing the measured absorption or machine reading of the sample between two measurements made on calibration solutions of neighbouring concentrations within the optimum working range.

Calibration function: function relating atomic absorption instrument readings, either in absorption or in other machine units, to the concentration of lead or cadmium which generated the instrument reading lead stock solution.

B.3 Reagents

All reagents shall be of recognized analytical grade.

B.3.1 Lead stock solution.

Prepare analytical stock solutions containing 1 000 mg ± 1 mg of lead per litre.

Alternatively, an appropriate commercially available standardized lead AAS solution may be used.

B.3.2 Cadmium stock solution.

Prepare analytical stock solutions containing 1 000 mg ± 1 mg of cadmium per litre.

Alternatively, an appropriate commercially available standardized cadmium AAS solution may be used.

B.3.3 Lead standard solution.

Produce a lead standard solution which is 100 mg/l Pb, or 0,1 g of lead per litre.

B.3.4 Cadmium standard solution.

Produce a cadmium standard solution which is 10 mg/l Cd, or 0,01 g of cadmium per litre.

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Standard solutions may be kept in suitable, aged, tightly closed containers (i.e. polyethylene) for 4 weeks without loss of quality. New containers may be aged by filling with standard solution and allowing to stand for 24 h. The aging solution is discarded.

Use one-mark glass pipettes or precision piston pipettes, typically 1 000 µl and 500 µl, and appropriate volumetric glassware (e.g. 500 ml to 2 000 ml) to prepare proper calibration solutions by dilution of the standard stock solutions with test solution.

Keep the solutions in suitable and aged containers. Renew these solutions every 4 weeks.

B.4 Apparatus

Atomic absorption spectrometer equipped with light sources (hollow cathode or electrodeless discharge lamps) specific for lead and cadmium, instrumental background correction, and a single slot (approximately 100 mm) or boiling burner head. Digital concentration readout may be used. Use air-acetylene (ethyne) flame and operating conditions recommended by the instrument manufacturer.

Using these conditions, characteristic concentration (concentration that gives 0,004 4 absorbance) should be approximately (±20 %) 0,2 mg/l for Pb measured at 217 nm.

Where appropriate, a wavelength of 283,3 nm may be used for the analytical confirmation of lead.

Characteristic concentration should be approximately (±20 %) 0,02 mg/l for Cd measured at 228,8 nm.

B.5 Procedures

B.5.1 Calibration

Set up the atomic absorption spectrometer according to the manufacturer's instructions using wavelengths of 217 nm for lead determination and 228,8 nm for cadmium determination with an appropriate correction for background absorption effects.

Where appropriate, a wavelength of 283,3 nm may be used for the analytical confirmation of lead.

Aspirate the zero concentration of the set of calibration solutions and adjust zero. Aspirate the set of calibration solutions, prepared by dilution of the standard solution with test solution (3.10), and prepare calibration curves over a linear range.

Suggested ranges: 0,2 mg/l Pb to 5 mg/l Pb; −0,05 mg/l Cd to 0,5 mg/l Cd.

B.5.2 Determination of lead and cadmium

Set up the spectrometer as described previously. Aspirate water (5.1.1) and then 4 % per volume acetic acid solution and verify that the absorbance is zero. Aspirate the extraction solution (3.7), interspersed with test solution (3.10) and record the absorbance values of the extraction solutions.

B.6 Expression of results

The lead or cadmium concentration, ρ_0, expressed in milligrams per litre of the extraction solution, is given by Formula (B.1):

$$\rho_0 = \frac{(A - A_1)}{(A_2 - A_1)} \times (\rho_2 - \rho_1) + \rho_1 \tag{B.1}$$

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where

A is the absorbance of the lead or cadmium in the extraction solution;

A_1 is the absorbance of the lead or cadmium in the lower bracketing solution;

A_2 is the absorbance of the lead or cadmium in the upper bracketing solution;

ρ_1 is the lead or cadmium concentration, in milligrams per litre, of the lower bracketing solution;

ρ_2 is the lead or cadmium concentration, in milligrams per litre, of the upper bracketing solution.

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Annex C

(informative)

Analytical method using ICP-OES

C.1 General

This annex describes an analytical method by ICP-OES for the determination of lead and cadmium in extraction solution.

C.2 Principles

Determination of lead and cadmium by ICP-OES consists of the following steps:

1) introduction of a measuring solution into a radiofrequency plasma to cause dissolution, atomization and ionization of elements;
2) production of characteristic emission spectra by a radiofrequency ICP;
3) dispersion of the spectra by a grating spectrometer and monitoring of the intensities of the lines with a detector;
4) processing of the signals from the detector using a data-handling system;
5) quantitative determination of the Pb and Cd after calibration with suitable calibration solutions.

C.3 Interferences

C.3.1 General

Several types of interference effects can contribute to inaccuracies in the determination of elements. They are also termed matrix effects.

Interferences can be classified as follows.

C.3.2 Spectral interferences

These types of interferences are caused by light of other elements present in the matrix. The error is additive. Typically, they cause an erroneously high reading. In the case of background influences, low readings can also occur. The most important spectral interferences for both Pb and Cd are listed in Table C.1.

Table C.1 — Recommended wavelengths and interfering elements for Pb and Cd

Element	Wavelength nm	Interfering element
Pb	220,353	Al, Co, Fe, Ti
	283,305	Cr, Fe
Cd	214,441	As, Cr, Fe, Sc, Sb
	226,502	As, Co, Fe, Ni
	228,802	As, Co, Sc

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