INTERNATIONAL STANDARD

ISO 6486-1

Third edition
2019-08

Ceramic ware, glass ceramic ware and glass dinnerware in contact with food — Release of lead and cadmium —

Part 1: **Test method**

Vaisselle en céramique, vaisselle en vitrocéramique et vaisselle de table en verre en contact avec les aliments — Émission de plomb et de cadmium —

Partie 1: Méthode d'essai

Reference number
ISO 6486-1:2019(E)

COPYRIGHT PROTECTED DOCUMENT

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Fax: +41 22 749 09 47
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Page

Foreword ... **iv**
Introduction ... **v**
1 Scope ... **1**
2 Normative references ... **1**
3 Terms and definitions ... **1**
4 Principles ... **3**
5 Reagents and materials ... **4**
5.1 Reagents ... 4
5.2 Materials and supplies ... 4
6 Apparatus ... **4**
6.1 Analytical techniques ... 4
6.2 Accessories ... 4
7 Sampling ... **5**
7.1 Priority ... 5
7.2 Sample size ... 5
7.3 Preparation and preservation of test samples ... 5
8 Procedures ... **5**
8.1 Determination of reference surface area for flatware ... 5
8.2 Preparation of articles which cannot be filled ... 5
8.3 Extraction ... 6
8.3.1 Extraction temperature ... 6
8.3.2 Leaching ... 6
8.3.3 Sampling of the extraction solution for analysis ... 6
8.3.4 Drinking rim test ... 6
8.4 Articles used in repeated contact with foodstuffs ... 6
9 Analytical methods ... **7**
9.1 General ... 7
9.2 Calculation of release of lead and cadmium from ceramic hollowware ... 7
9.3 Calculation of release of lead and cadmium from flatware ... 7
9.4 Calculation of release of lead and cadmium from drinking rim ... 7
10 Test report ... **7**
Annex A (informative) **Analytical method using ICP-MS** ... **9**
Annex B (informative) **Analytical method using FAAS** ... **17**
Annex C (informative) **Analytical method using ICP-OES** ... **20**
Bibliography ... **25**

Foreword

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

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

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

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

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

This document was prepared by Technical Committee ISO/TC 166, *Ceramic ware, glassware and glass ceramic ware in contact with food*.

This third edition cancels and replaces the second edition (ISO 6486-1:1999), which has been technically revised. The main changes to the previous edition are as follows:

— technical procedures updated and permissible limits for metal release 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 6486 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.

Introduction

Release of potentially toxic metals, particularly lead and cadmium, from ceramic and 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 ceramic, glass-ceramic and glass dinnerware used for the preparation, cooking, 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 ceramic ware present non-tariff barriers to international trade in these commodities. Accordingly, there is a need to maintain internationally accepted methods of testing ware for the release of potentially toxic metals.

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 to be 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 6486-2 are set on the basis of a single extraction into the extraction solution. This document 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 6486-2. New limits that are appropriate to third extraction data are currently being agreed.

Ceramic ware, glass ceramic ware and glass dinnerware in contact with food — Release of lead and cadmium —

Part 1: Test method

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 ceramic ware, glass ceramic ware and glass dinnerware intended to be used in contact with food, but excluding vitreous and porcelain enamel articles (covered by ISO 4531).

This document is applicable to ceramic ware, glass ceramic ware and glass dinnerware which is intended to be used for the preparation, cooking, serving and storage of food and beverages, excluding all articles used in food manufacturing industries or in which food is sold.

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
reference 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 item, measured downwards from the upper edge along the wall of the item

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

3.11
ceramic ware
ceramic articles which are intended to be used in contact with foodstuffs, for example *foodware* (3.16) made of china, porcelain and earthenware, whether glazed or not

3.12
cup
small glass or *ceramic hollowware* (3.19) of approximately 240 ml capacity with a handle, commonly used for consumption of beverages, for example coffee or tea, at elevated temperature

Note 1 to entry: Cups typically have curved sides and are generally used with a saucer.

3.13
mug
small glass or *ceramic hollowware* (3.19) of approximately 240 ml capacity with a handle, commonly used for consumption of beverages, for example coffee or tea, at elevated temperature

Note 1 to entry: Mugs typically have cylindrical sides.

3.14
dinnerware
combination of ceramic ware, *glass ceramic ware* (3.18) and glass ware specially intended for the serving of food on the table, including plates, dishes and salad bowls, but excluding ware typically used for beverages

3.15
flatware
ceramic or *glassware* (3.17) which has an internal depth not exceeding 25 mm, measured from the lowest point to the horizontal plane passing through the point of overflow

3.16
foodware
articles which are intended to be used for the preparation, cooking, serving and storage of food or drinks

3.17
glassware
articles which are intended to be used in contact with foodstuffs 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. The material may be clear, coloured or opaque, depending on the level of colouring and opacifying agents used.

3.18
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.

3.19
ceramic hollowware
ceramic ware which 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: Hollowware is subdivided into three categories based on volume:

— small: hollowware with a capacity of < 1,1 l;

— large: hollowware with a capacity of ≥ 1,1 l;

— storage: hollowware with a capacity of ≥ 3 l.

4 Principles

Ceramic ware, glass ceramic ware 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 samples.

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 lead and cadmium to be measured. In the case of ICP-OES, see the methodology described in Annex C for additional information.

5 Reagents and materials

5.1 Reagents

All reagents shall be of recognized analytical grade.

For the determination of lead and cadmium at trace and ultra trace 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.

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

5.1.2 Acetic acid, (CH_3COOH), glacial, ρ = 1,05 g/ml. Acetic acid purity better than 99 %, with Pb and Cd only at trace level.

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 50 °C to 57 °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 or 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.

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 at a hand-hot temperature using tap water containing a non-acidic 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.

8 Procedures

8.1 Determination of reference surface area for flatware

For circular articles, the reference surface area shall be calculated from the diameter of the article.

For others cases, place a specimen on a sheet of smooth paper and draw a contour around the rim. Determine the enclosed area by a suitable means. One recommended method is to cut out and weigh the enclosed area and to determine the area by comparison of the weight with the weight of a rectangular sheet of known area. Record this area, S_R, in square decimetres to two decimal places.

8.2 Preparation of articles which cannot be filled

Articles shall be filled to within 6 mm of overflowing as measured along the sloping side of flatware, or to within 1 mm of the rim as measured vertically for hollowware. Articles which cannot be filled in this manner to produce an acid depth at the deepest point of at least 5 mm are defined as non-fillable. Articles of this type may be tested by one of the following methods.

a) Standard articles may be fitted into a silicone rubber mould which forms a water-tight seal with the article and which encroaches no more than 6 mm from the rim and forms a depth of at least 5 mm but no more than 25 mm. Specimens prepared in this way are tested as fillable flatware articles.

b) A bead of silicone sealant may be formed around the edge of the article to permit filling of the article to a depth of at least 5 mm but no more than 25 mm. The bead shall encroach no more than 6 mm from the rim of the article. Specimens prepared in this way are tested as fillable flatware articles.

c) The article may be coated on all surfaces except the reference surface with melted paraffin wax and subsequently tested by immersion in test solution. Specimens prepared in this way are tested as non-fillable flatware articles.

8.3 Extraction

8.3.1 Extraction temperature

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

8.3.2 Leaching

8.3.2.1 Fillable articles

Fill each specimen with test solution (5.1.3) to within 1 mm of overflowing measured vertically for hollowware or 6 mm from overflowing as measured along the surface of flatware. For flatware determinations measure and record the volume of the test solution (5.1.3) used to fill the article. Cover the specimen.

Leach for (24 ± 0,5) h depending on the case studied.

8.3.2.2 Non-fillable articles

These articles, which have been masked with paraffin wax according to 8.2 c) are placed in a suitable vessel such as borosilicate glass of suitable size and test solution (5.1.3) is added in sufficient quantity to completely cover the sample. Record the amount of test solution (5.1.3) added to an accuracy of 2 %.

Leach for (24 ± 0,5) h depending on the case studied.

8.3.3 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.

8.3.4 Drinking rim test

Cups, mugs or other ceramic 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 of between 1,25 times and 2 times that of the cup. Add sufficient test solution (5.1.3) to the glassware container to fill to the 20 mm mark on the cup. Leave to stand for (24 ± 0,5) h, depending on the case considered, at (22 ± 2) °C and protect from excessive evaporation. 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. Determine lead and cadmium by the appropriate analytical methodology.

8.4 Articles used in repeated contact with foodstuffs

When an article is intended to come into repeated contact with foodstuffs, 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. 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 ceramic 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 flatware

The lead or cadmium released per unit area from flatware, R_0, expressed in micrograms per square decimetre, is given by Formula (1):

$$R_0 = \frac{\rho_0 \times V}{S_R} \tag{1}$$

where

ρ_0 is the lead or cadmium concentration, expressed in micrograms per litre, of the sample extract solution;

V is the filling volume of the specimen, expressed in litres;

S_R is the reference surface area of the article, expressed in square decimetres.

9.4 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.

10 Test report

The test report shall include the following information:

a) reference to this document, i.e. ISO 6486-1, 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: the surface area or the reference surface area, and the filling volume or contact volume for non-fillable articles and test specimens;

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;

f) the test results, expressed as individual values for each specimen and the mean value for identical test sample groups. For flatware items, also report the determined lead and cadmium concentration in the test solutions;

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

h) any unusual features observed.

Annex A
(informative)

Analytical method using ICP-MS

A.1 General

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

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 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

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_2O_2H	$^{94}Zr^{16}O^{1}H$ $^{95}Mo^{16}O$
	113	**12,2**	**In**	MoO, ZrOH, Ca_2O_2H, Ar_2O_2H, 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 shall 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.

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 1000 mg/l separately or together, if suitable, into a 1000 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 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.

The choice of elements for the internal standard 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.

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 solution 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 solution 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 document 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 or tune solution.

The optimization 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.

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 set up

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 (Table A.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) is acceptable.

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

$$L_D = b_{ave} + 3s_b \tag{A.1}$$

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)].

$$L_Q = b_{ave} + Fs_b \tag{A.2}$$

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.

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 the 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.

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	$\overline{x}$ µg/l	σ_R µg/l	Reproducibility CV %	σ_r µg/l	Repeatability CV %
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

l: Number of laboratories

n: Number of values

$\overline{x}$: 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[a] µg/l
4 % per volume acetic acid solution	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.

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.

Standard solution 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 with a fixed stroke, 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.

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

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

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 % acetic acid 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, $\rho 0$, expressed in micrograms per litre of the extraction solution, is given by Formula (B.1).

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

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 micrograms per litre, of the lower bracketing solution;

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

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

Because of the differences between various models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst will need to refer to the instructions provided by the manufacturer of the particular instrument.

If the peak shape changes in comparison with the peak shape generated by a single element solution, line overlap could be the reason. Background changes are best identified by overlaying spectra of blank, standards and samples. Also, the comparison of results for a given element measured at different lines will indicate spectral interferences.

C.3.3 Non-spectral interferences

C.3.3.1 Physical interferences

These are generally considered to be effects associated with the sample nebulization and other transport processes of the sample from the sample container to the plasma.

They are caused by the change in viscosity, density and/or surface tension. They may result in significant errors, especially in samples containing high dissolved solids and/or acid concentrations. These types of interferences can be reduced by matrix-matching (if the concentrations of the analytes are high enough, dilution of the sample may be the preferred way), the use of an internal standard (provided no excitation interferences are encountered) and/or utilization of the method of standard addition.

C.3.3.2 Excitation interferences

Depending on the relation of the room (operating) temperature to the plasma temperature, the change of the plasma temperature due to the introduction of sample may cause an increase or decrease of the signal. In addition, elements which readily release electrons may change the electron density in the plasma, which may influence the distribution between atomic and ionic transitions. Alkaline metals (Li, K, Na) are highly susceptible to excitation interferences, particularly on axial viewing. This interference can be reduced by keeping the room temperature at 22 °C ± 2 °C.

C.3.3.3 Chemical interferences

They are characterized by molecular compound formation, variation of oxidation state and solute vaporization effects. These interferences are very rare. However, when encountered, they may cause serious errors.

C.3.3.4 Detecting non-spectral interferences

In order to detect the non-spectral interferences, recovery experiments should be performed.

1) Dilution

   If the analyte concentration is sufficiently high (at least a factor of 10 above the instrumental detection limit after dilution), the results of the analysis of a dilution needs to agree within ±10 % of those obtained from the undiluted sample (or within some acceptable control limit that has been established for that matrix).

2) Standards additions (spike recovery)

   The recovery of a spike addition added at a minimum level of ten times the instrumental detection limit (maximum 100 times) to the original determination needs to be within 80 % to 120 % or within the established control limit for that matrix. If not, there could be a matrix effect.

The use of a standard addition analysis procedure can usually compensate for non-spectral interferences.

C.3.3.5 Compensation of non-spectral interferences by the use of internal standards

The use of internal standards is in some cases a suitable method to correct for interferences. The approach involves the addition of a known amount of a substance or material to the sample. The sample is then analysed and the responses for the determinant and the added (internal) standard are measured. The observation for the internal standard is then used to relate the determinant signal to the determinant concentration. The effect on analytical error and the type of likely error will vary according to the exact approach adopted.

Usually, there is an initial, conventional calibration relating the responses for all elements to their concentrations. Consequently, each subsequent analysis depends on the internal standard as a means of adjusting for changes in instrumental sensitivity, possibly caused by changes in sample uptake or by drift in detector response. Here, care needs to be taken to eliminate factors (such as the efficiency of excitation) which affect the standard and one or more of the determinants to different extents since these will lead to systematic error. Unless the size of response for the internal standard is the same as that for all elements of interest (which is most unlikely), nonlinearity of response can also lead to error. This may well go undetected, since it is rare to make a range of internal standard additions.

As a consequence, this calibration approach will increase the random error by the random variation associated with the internal standardization. However, overall precision may still be preferable, since the consequent control over, for example, drift could improve the observed total standard deviation.

C.4 Reagents

All reagents shall be of recognized analytical grade.

For the determination of elements at trace and ultra-trace level, use reagents 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.

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

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

C.4.3 Acetic acid test solution, 4 % per volume.

Add 40 ml of acetic acid (C.3.2) to water (C.3.1) 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.

C.4.4 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 analyte of 1 000 mg/I are suitable. These solutions are considered to be stable for one year, but in reference to guaranteed stability, the recommendations of the manufacturer should be considered.

C.4.5 Lead and cadmium standard solution: ρ (Pb) = 100 mg/l – ρ (Cd) = 100 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 100 ml one-mark volumetric flask (6.2.5). Bring to volume with test solution (C.3.3) and transfer to a suitable storage bottle.

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

C.4.6 Internal standard solution.

The choice of elements for internal standard solution depends on the sample matrix. The internal standard element cannot be present or should be negligibly low in the blank, samples and standards. In addition, the internal standard element and the analyte should behave similarly in the plasma.

Y (Yttrium) can be suitable for this purpose.

A suitable concentration range of the internal standard in samples and calibration solutions is 1 mg/l to 10 mg/l.

C.4.7 Lead and cadmium calibration solution.

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

Prepare the calibration solutions that cover the required working range by diluting the element standard solutions with an adequate volume of 4 % per volume acetic acid solution 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 an adequate internal standard solution before bringing up to volume.

C.4.8 Calibration blank solution.

The calibration blank solution is prepared in the same way as the calibration solutions, but the analyte is left out. Prepare the calibration blank solution by adding an adequate volume of 4 % per volume acetic acid solution to make the composition of the calibration blank solution equal to the composition of the test sample. If necessary, add an adequate internal standard solution before bringing up to volume.

C.4.9 Calibration check solution.

The calibration check solution is a solution of known composition within the range of the calibration solutions. It is prepared from a standard source different from that of the calibration standards. The solution should be prepared in the same acid composition (matrix) of the calibrations and the test samples.

C.5 Apparatus

C.5.1 Inductively coupled plasma optic emission spectrometer

ICP-OES system includes:

— sample introduction system (pump, nebulizer, spray chamber);

— inductively coupled plasma (radio-frequency generator, load coil, torch);

— computer-controlled emission spectrometer with background correction;

— argon gas supply – high purity grade, i.e. > 99,99 %.

C.5.2 Accessories

The stability of test samples and calibration solutions depends to a high degree on the container material. The materials shall be checked according to the specific purpose. For the determination of lead and cadmium in acetic acid 4 % (v/v) leachates, HDPE or 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 (C.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.

C.6 Procedures

C.6.1 Instrument set up

Follow the instructions to adjust the instrumental parameters of the ICP-OES according to the manufacturer's manual.

Set up the instrument with the proper operating parameters established from the manufacturer's instruction manual. Allow the instrument to achieve thermal stability before beginning.

Initiate the appropriate operating configuration of the computer.

C.6.2 Calibration and determination of Pb and Cd

Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the lead and cadmium calibration solutions (C.4.7).

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

The working range should be above the LOQ. Suggested ranges: 0,05 mg/l Pb to 20,0 mg/l Pb; 0,005 mg/l Cd to 2,0 mg/l Cd.

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

For work on a daily basis, to set up the calibration curve, one blank solution and two calibration solutions (an upper concentration calibration solution and a lower concentration calibration solution) are sufficient. When working with two calibration standards, control the calibration function against samples with a calibration check solution as if it were a sample. Ensure that the concentration values do not deviate from the actual values by more than ± 5 % (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

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

— Establish a calibration graph by the emission signals from calibration blank and calibration solutions.

— Determine the mass concentrations of samples with the aid of the emissions and the calibration graphs.

— Correct the results, taking into account the mass concentrations from the blank calibration solutions, and incorporate all dilution steps in the calculation.

— Analyse a calibration check solution (C.4.9) and the calibration blank solution (C.4.8) every 25 samples.

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.

C.6.3 Expression of results

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

Bibliography

[1] ISO 4531, *Vitreous and porcelain enamels — Release from enamelled articles in contact with food — Methods of test and limits*

[2] ISO 6486-2, *Ceramic ware, glass-ceramic ware and glass dinnerware in contact with food — Release of lead and cadmium — Part 2: Permissible limits*

[3] ISO 8288, *Water quality — Determination of cobalt, nickel, copper, zinc, cadmium and lead — Flame atomic absorption spectrometric methods*

[4] ISO 8391-1, *Ceramic cookware in contact with food — Release of lead and cadmium — Part 1: Method of test*

[5] ISO 11885, *Water quality — Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)*

[6] ISO 17294-1, *Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS) — Part 1: General guidelines*

[7] European directive 69/493/EEC Council Directive 69/493/EEC of 15 December 1969 on the approximation of the laws of the Member States relating to crystal glass

[8] "Scoping study on the release of metals from crystalware (in support of the revision of Ceramic Directive 84/500/EEC)," Mercedes Ana Peltzer, Giorgia Beldì, Natalia Jakubowska and Catherine Simoneau. Luxembourg: Publications Office of the European Union 2015

[9] "Scoping investigations on the release of metals from the rim area of decorated articles (in support of the revision of Ceramic Directive 84/500/EEC)," Mercedes Ana Peltzer, Giorgia Beldì, Natalia Jakubowska and Catherine Simoneau. Luxembourg: Publications Office of the European Union 2015

[10] "Report of two Inter-laboratory comparisons from the European Reference Laboratory for Food Contact Materials - Elements from Food Contact Materials: ILC 03 2014 – Plastics and ILC 04 2014 – Ceramics," Giorgia Beldì, Mercedes Peltzer and Catherine Simoneau. Luxembourg: Publications Office of the European Union, 2015

[11] "Study on the Release of Metals from Ceramics and Glass/Crystalware in Support of the Revision of Ceramic Directive 84/500/EEC - Part 1: Release of Metals from Ceramic Articles," Peltzer Mercedes, Beldì Giorgia, Jakubowska Natalia, Simoneau Catherine EUR 27179 EN, Luxembourg: Publications Office of the European Union, 2015

[12] "Precision criteria of methods for the quantification of metals migrated from Food Contact Materials: Pre-validation data derived from ILCs on elements representative for plastics and ceramics," Giorgia Beldì, Natalia Jakubowska and Catherine Simoneau EUR 27827 EN, JRC100838, Luxembourg: Publications Office of the European Union, 2016

[13] "Testing approaches for the release of metals from ceramic articles - In support of the revision of the Ceramic Directive 84/500/EEC," Giorgia Beldì, Jakubowska Natalia, Mercedes Peltzer and Catherine Simoneau EUR 28363 EN, Luxembourg: Publications Office of the European Union, 2016

[14] "Report on the inter-laboratory comparison exercise organised by the European Union Reference Laboratory for Food Contact Materials - Determination of elements in acetic acid solutions and in migration from ceramic and glass tableware," Jakubowska Natalia, Giorgia Beldì, Catherine Simoneau and Eddo Hoekstra EUR 28690 EN, Luxembourg: Publications Office of the European Union, 2017

[15] "Towards suitable tests for the migration of metals from ceramic and crystal tableware: Work in support of the revision of the Ceramic Directive 84/500/EEC", Catherine Simoneau, Giorgia

Beldì, Jakubowska Natalia, Mercedes Peltzer EUR 28872 EN, Luxembourg: Publications Office of the European Union, 2017

ICS 67.250; 81.060.20; 81.040.30; 97.040.60

Price based on 26 pages