BS EN 62321-5:2014

BSI Standards Publication

Determination of certain substances in electrotechnical products

Part 5: Cadmium, lead and chromium in polymers and electronics and cadmium and lead in metals by AAS, AFS, ICP-OES and ICP-MS

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National foreword

This British Standard is the UK implementation of EN 62321-5:2014. It is identical to IEC 62321-5:2013. Together with BS EN 62321-1:2013, BS EN 62321-2:2014, BS EN 62321-3-1:2014, BS EN 62321-3-2:2014, BS EN 62321-4:2014, BS EN 62321-6, BS EN 62321-7-1, BS EN 62321-7-2 and BS EN 62321-8 it supersedes BS EN 62321:2009, which will be withdrawn upon publication of all parts of the BS EN 62321 series.

The UK participation in its preparation was entrusted to Technical Committee GEL/111, Electrotechnical environment committee.

A list of organizations represented on this committee can be obtained on request to its secretary.

Published by BSI Standards Limited 2014

ISBN 978 0 580 71850 2
ICS 13.020; 43.040.10

This British Standard was published under the authority of the Standards Policy and Strategy Committee on 31 May 2014.

Amendments/corrigenda issued since publication

Date	Text affected

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 62321-5

April 2014

ICS 13.020; 43.040.10

Supersedes EN 62321:2009 (partially)

English version

Determination of certain substances in electrotechnical products - Part 5: Cadmium, lead and chromium in polymers and electronics and cadmium and lead in metals by AAS, AFS, ICP-OES and ICP-MS
(IEC 62321-5:2013)

Détermination de certaines substances dans les produits électrotechniques -
Partie 5: Du cadmium, du plomb et du chrome dans les polymères et les produits électroniques, du cadmium et du plomb dans les métaux par AAS, AFS, ICP-OES et ICP-MS
(CEI 62321-5:2013)

Verfahren zur Bestimmung von bestimmten Substanzen in Produkten der Elektrotechnik -
Teil 5: Cadmium, Blei und Chrom in Polymeren und Elektronik und Cadmium und Blei in Metallen mit AAS, AFS, ICP-OES und ICP-MS
(IEC 62321-5:2013)

This European Standard was approved by CENELEC on 2013-11-15. CENELEC members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration.

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CENELEC

European Committee for Electrotechnical Standardization
Comité Européen de Normalisation Electrotechnique
Europäisches Komitee für Elektrotechnische Normung

CEN-CENELEC Management Centre: Avenue Marnix 17, B - 1000 Brussels

Ref. No. EN 62321-5:2014 E

Foreword

The text of document 111/297/FDIS, future edition 1 of IEC 62321-5, prepared by IEC/TC 111 "Environmental standardization for electrical and electronic products and systems" was submitted to the IEC-CENELEC parallel vote and approved by CENELEC as EN 62321-5:2014.

The following dates are fixed:

• latest date by which the document has to be implemented at national level by publication of an identical national standard or by endorsement	(dop)	2014-10-25
• latest date by which the national standards conflicting with the document have to be withdrawn	(dow)	2016-11-15

EN 62321-5:2014 is a partial replacement of EN 62321:2009, forming a structural revision and generally replacing Clauses 8 to 10, as well as Annexes F, G and H.

Future parts in the EN 62321 series will gradually replace the corresponding clauses from EN 62321:2009. Until such time as all parts are published, however, EN 62321:2009 remains valid for those clauses not yet re-published as a separate part.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CENELEC [and/or CEN] shall not be held responsible for identifying any or all such patent rights.

Endorsement notice

The text of the International Standard IEC 62321-5:2013 was approved by CENELEC as a European Standard without any modification.

Annex ZA
(normative)

Normative references to international publications with their corresponding European publications

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

NOTE When an international publication has been modified by common modifications, indicated by (mod), the relevant EN/HD applies.

Publication	Year	Title	EN/HD	Year
IEC 62321-1	-	Determination of certain substances in electrotechnical products - Part 1: Introduction and overview	EN 62321-1	-
IEC 62321-2	-	Determination of certain substances in electrotechnical products - Part 2: Disassembly, disjunction and mechanical sample preparation	EN 62321-2	-
IEC 62321-3-1	-	Determination of certain substances in electrotechnical products - Part 3-1: Screening electrotechnical products for lead, mercury, cadmium, total chromium and total bromine using X-ray Fluorescence Spectrometry	EN 62321-3-1	-
ISO 3696	-	Water for analytical laboratory use - Specification and test methods	EN ISO 3696	-
ISO 5961	-	Water quality - Determination of cadmium by atomic absorption spectrometry	EN ISO 5961	-

CONTENTS

INTRODUCTION

The widespread use of electrotechnical products has drawn increased attention to their impact on the environment. In many countries this has resulted in the adaptation of regulations affecting wastes, substances and energy use of electrotechnical products.

The use of certain substances (e.g. lead (Pb), cadmium (Cd) and polybrominated diphenyl ethers (PBDE's)) in electrotechnical products, is a source of concern in current and proposed regional legislation.

The purpose of the IEC 62321 series is therefore to provide test methods that will allow the electrotechnical industry to determine the levels of certain substances of concern in electrotechnical products on a consistent global basis.

WARNING – Persons using this International Standard should be familiar with normal laboratory practice. This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

DETERMINATION OF CERTAIN SUBSTANCES IN ELECTROTECHNICAL PRODUCTS –

Part 5: Cadmium, lead and chromium in polymers and electronics and cadmium and lead in metals by AAS, AFS, ICP-OES and ICP-MS

1 Scope

This Part of IEC 62321 describes the test methods for lead, cadmium and chromium in polymers, metals and electronics by AAS, AFS, ICP-OES and ICP-MS.

This standard specifies the determination of the levels of cadmium (Cd), lead (Pb) and chromium (Cr) in electrotechnical products. It covers three types of matrices: polymers/polymeric workpieces, metals and alloys and electronics.

This standard refers to the sample as the object to be processed and measured. What the sample is or how to get to the sample is defined by the entity carrying out the tests. Further guidance on obtaining representative samples from finished electronic products to be tested for levels of regulated substances may be found in IEC 62321-2. It is noted that the selection and/or determination of the sample may affect the interpretation of the test results.

This standard describes the use of four methods, namely AAS (atomic absorption spectrometry), AFS (atomic fluorescence spectrometry), ICP-OES (inductively coupled plasma optical emission spectrometry), and ICP-MS (inductively coupled plasma mass spectrometry) as well as several procedures for preparing the sample solution from which the most appropriate method of analysis can be selected by experts.

As the hexavalent-Cr analysis is sometimes difficult to determine in polymers and electronics, this standard introduces the screening methods for chrome in polymers and electronics except from AFS. Chromium analysis provides information about the existence of hexavalent-Cr in materials. However, elemental analyses cannot selectively detect hexavalent-Cr; it determines the amount of Cr in all oxidation states in the samples. If Cr amounts exceed the hexavalent-Cr limit, testing for hexavalent-Cr should be performed.

The test procedures described in this standard are intended to provide the highest level of accuracy and precision for concentrations of Pb, Cd and Cr that range, in the case of ICP-OES and AAS, from 10 mg/kg for Pb, Cd and Cr, in the case of ICP-MS, from 0,1 mg/kg for Pb and Cd in the case of AFS, the range is from 10 mg/kg for Pb and 1.5 mg/kg for Cd. The procedures are not limited for higher concentrations.

This standard does not apply to materials containing polyfluorinated polymers because of their stability. If sulfuric acid is used in the analytical procedure, there is a risk of losing Pb, thus resulting in erroneously low values for this analyte. In addition, sulfuric acid and hydrofluoric acid are not suitable for determining Cd by AFS, because it disturbs the reduction of Cd.

Limitations and risks occur due to the solution step of the sample, e.g. precipitation of the target or other elements may occur, in which case the residues have to be checked separately or dissolved by another method and then combined with the test sample solution.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

IEC 62321-1, *Determination of certain substances in electrotechnical products – Part 1: Introduction and overview*[1]

IEC 62321-2, *Determination of certain substances in electrotechnical products – Part 2: Disassembly, disjointment and mechanical sample preparation*[1]

IEC 62321-3-1, *Determination of certain substances in electrotechnical products – Part 3-1: Screening – Lead, mercury, cadmium, total chromium and total bromine using X-ray fluorescence spectrometry*[1]

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

ISO 5961, *Water quality – Determination of cadmium by atomic absorption spectrometry*

3 Terms, definitions and abbreviations

3.1 Terms and definitions

For the purposes of this document, the terms and definitions given in IEC 62321-1, as well as the following, apply.

3.1.1
accuracy
closeness of agreement between a test result and an accepted reference value

3.1.2
calibration standard
substance in solid or liquid form with known and stable concentration(s) of the analyte(s) of interest used to establish instrument response (calibration curve) with respect to analyte(s) concentration(s)

3.1.3
calibration solution
solution used to calibrate the instrument prepared either from (a) stock solution(s) or from a (certified) reference material

3.1.4
certified reference material
reference material, accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities using valid procedures

3.1.5
laboratory control sample
known matrix spiked with compound(s) representative of the target analytes, used to document laboratory performance

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[1] To be published.

[Based on US EPA SW-846] [1] [2]

3.1.6

reagent blank solution

prepared by adding to the solvent the same amounts of reagents as those added to the test sample solution (same final volume)

3.1.7

test sample solution

solution prepared with the test portion of the test sample according to the appropriate specifications such that it can be used for the envisaged measurement

3.2 Abbreviations

CCV	continuing calibration verification
LCS	laboratory control sample

4 Reagents

4.1 General

For the determination of elements at trace level, the reagents shall be of adequate purity. The concentration of the analyte or interfering substances in the reagents and water shall be negligible compared to the lowest concentration to be determined.

All reagents for ICP-MS analysis, including acids or chemicals used shall be of high-purity: trace metals shall be less than 1×10^{-6} % in total.

For measurements by ICP-OES and ICP-MS, the memory effect occurs in cases where high concentrations of elements are introduced. Dilution of the sample solution is required for high levels of each element. If the memory effect is not decreased by dilution, thorough washing of the equipment is required.

4.2 Reagents

The following reagents are used:

a) Water: Grade 1 specified in ISO 3696 used for preparation and dilution of all sample solutions.

b) Sulfuric acid:
   1) Sulfuric acid: $\rho(H_2SO_4)$ = 1,84 g/ml, a mass fraction of 95 %, “trace metal” grade.
   2) Sulfuric acid: dilution (1:2): dilute 1 volume of concentrated sulfuric acid (4.2 b 1)) with 2 volumes of water (4.2 a))

c) Nitric acid:
   1) Nitric acid: $\rho(HNO_3)$ = 1,40 g/ml, a mass fraction of 65 %, “trace metal” grade.
   2) Nitric acid, a mass fraction of 10 %, “trace metal” grade.
   3) Nitric acid: 0,5 mol/l, “trace metal” grade.
   4) Nitric acid: dilution (1:2): dilute 1 volume of concentrated nitric acid (4.2.c 1)) with 2 volumes of water (4.2 a))

d) Hydrochloric acid:
   1) Hydrochloric acid, $\rho(HCl)$ = 1,19 g/ml, a mass fraction of 37 %, “trace metal” grade.

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[2] Figures in square brackets refer to the Bibliography.

   2) Hydrochloric acid: dilution (1:2): dilute 1 volume of concentrated hydrochloric acid (4.2.d) 1)) with 2 volumes of water (4.2 a))
   3) Hydrochloric acid, a mass fraction of 5 %, “trace metal” grade.
   4) Hydrochloric acid, a mass fraction of 10 %, “trace metal” grade.

e) Hydrofluoric acid: $\rho(HF)$ = 1,18 g/ml, a mass fraction of 40 %, “trace metal” grade.

f) Fluoroboric acid: HBF_4, a mass fraction of 50 %, “trace metal” grade.

g) Perchloric acid: $\rho(HClO_4)$ =1,67 g/ml, a mass fraction of 70 %, “trace metal” grade.

h) Phosphoric acid: $\rho(H_3PO_4)$ =1,69 g/ml, more than a mass fraction of 85 %, “trace metal” grade.

i) Hydrobromic acid: $\rho(HBr)$ = 1,48 g/ml, a mass fraction of 47 % to 49 %, “trace metal” grade.

j) Boric acid (H_3BO_3): 50 mg/ml, a mass fraction of 5 %, “trace metal” grade.

k) Hydrogen peroxide: $\rho(H_2O_2)$ = 1,10 g/ml, a mass fraction of 30 %, “trace metal” grade.

l) Mixed acid:
   1) Mixed acid 1, two parts hydrochloric acid (4.2 d) 1)), one part nitric acid (4.2 c)1)) and two parts water (4.2 a)).
   2) Mixed acid 2, one part nitric acid (4.2 c) 1)) and three parts hydrofluoric acid (4.2 e)).
   3) Mixed acid 3, three parts hydrochloric acid (4.2 d) 1)) and one part nitric acid (4.2 c)1)).

m) Potassium hydroxide (KOH), “trace metal” grade.

n) Potassium borohydride (KBH_4), “trace metal” grade.

o) Potassium ferricyanide ($K_3(Fe(CN)_6)$), “trace metal” grade.

p) Oxido – reduction agent: a mass fraction of 1,5 % KBH_4 – a mass fraction of 1 % $K_3(Fe(CN_6)$ in a mass fraction of 0,2 % KOH.

   Add approximately 800 ml of water (4.2 a)) to a 1 000 ml volumetric flask (5.2 e)3)) followed by the addition of 2 g potassium hydroxide (4.2 m)). Add 15 g potassium borohydride (4.2 n)) and 10 g potassium ferricyanide (4.2 o)), stir to dissolve. Fill up to the mark with water (4.2 a)). Prepare daily.

q) Reducing agents:
   1) Reducing agent 1, a mass fraction of 3 % KBH_4 in a mass fraction of 0,2 % KOH:

      Add approximately 800 ml of water (4.2 a)) to a 1 000 ml volumetric flask (5.2 e) 3)) followed by the addition of 2 g potassium hydroxide (4.2 m)). Add 30 g of potassium borohydride (4.2 n)), stir to dissolve. Fill up to the mark with water (4.2 a)). Prepare daily.

   2) Reducing agent 2, a mass fraction of 4 % KBH_4 in a mass fraction of 0,8 % KOH.

      Add approximately 800 ml of water (4.2 a)) to a 1 000 ml volumetric flask (5.2 e) 3)), followed by the addition of 8 g potassium hydroxide (4.2 m)). Add 40 g of potassium borohydride (4.2 n)), stir to dissolve. Fill up to the mark with water (4.2 a)). Prepare daily.

r) Carrier flow:
   1) Carrier flow 1, a mass fraction of 1,5 % HCl.
   2) Carrier flow 2, a mass fraction of 1 % HCl.

s) Thiourea ($(NH_2)_2CS$) solution, a mass fraction of 10 % . Prepare daily.

t) Masking agent:
   1) Masking agent 1, a mass fraction of 5 % oxalic acid – a mass fraction of 5 % potassium sulfocyanate (KSCN) – a mass fraction of 0,5 % o-phenanthroline ($C_{12}H_8N_2$) solution:

      Add 10 g oxalic acid, 10 g potassium sulfocyanate and 1 g o-phenanthroline to 200 ml of water (4.2 a)). Heat at low temperature and stir to dissolve, taking care to avoid boiling of the solution. Use the solution before the solid crystallizes out. Discard the solution when it becomes dark and prepare a fresh one.

2) Masking agent 2, a mass fraction of thiourea 10 % – ascorbic acid a mass fraction of 10 % solution.

   Dissolve 10 g thiourea and 10 g ascorbic acid in 100 ml of water. Prepare daily.

u) Cobalt solution, 50 mg/l.

v) Stock solution:
   1) Stock solution with 1 000 mg/l of Pb.
   2) Stock solution with 1 000 mg/l of Cd.
   3) Stock solution with 1 000 mg/l of Cr.
   4) Stock solution with 10 000 mg/l of Fe.
   5) Stock solution 10 000 mg/l of Cu.

w) Internal standard stock solution.
   1) Internal standard elements that do not interfere with the target element are used for ICP-OES and ICP-MS. Also, the presence of these internal standard elements in the sample solution shall be at negligible levels. Sc, In, Tb, Lu, Re, Rh, Bi and Y may be used as internal standard elements.
   2) For use with ICP-OES, Sc or Y is recommended. The recommended concentration is 1 000 mg/l.
   3) For use with ICP-MS, Rh is recommended. The recommended concentration is 1 000 μg/l.

The toxicity of each reagent in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals at the lowest possible level by whatever means available is recommended.

Preparation methods involve the use of strong acids, which are corrosive and cause burns. Laboratory coats, gloves and safety glasses should be worn when handling acids.

Nitric acid gives off toxic fumes. Always carry out digestion in a fume cupboard, and also when adding acid to samples because of the possibility of toxic gases being released.

The exhaust gases from the plasma should be ducted away by an efficient fume extraction system.

Special precautionary measures should be taken when hydrofluoric acid is used, i.e. HF antidote gel (2,5 % calcium gluconate in a water-soluble gel) for first aid treatment of HF burns on the skin.

Analytical grade reagents may be used as an alternative except when utilizing ICP-MS methods.

5 Apparatus

5.1 General

In general, the collection and storage of glassware are critical parts of trace analysis, regardless of the type of sample to be analysed. Because of the sensitivity of the Pb, Cd and Cr analysis techniques described, each individual sampling step shall be carried out with great care. All sampling, storage and manipulation apparatus shall be metal-free. Soak all glassware in 10 % nitric acid (4.2 c) 2)) for 24 h at room temperature, and then rinse thoroughly with water (4.2 a)).

5.2 Apparatus

The following equipment shall be used:

a) Analytical balance: capable of measuring accurately to 0,000 1 g.

b) HF-resistant sample introduction system: system in which the sample insertion section and torch have been treated for resistance to HF.

c) Argon gas: gas with purity of over 99,99 %.

d) Acetylene gas: gas with purity of over 99,99 %.

e) Glassware: all glassware shall be cleaned with 10 % nitric acid (4.2 c) 2)) before use:

   1) Kjeldahl flask: 100 ml;

   2) Beakers: such as 100 ml, 200 ml, 500 ml etc.;

   3) Volumetric flasks: such as 50 ml, 100 ml, 200 ml, 500 ml, 1 000 ml, etc. Where appropriate, other types of volumetric equipment with acceptable precision and accuracy can be used as an alternative to volumetric flasks.

   4) Pipettes: such as 1 ml, 5 ml, 10 ml, 20 ml, etc.;

   5) Watch glass.

f) Crucibles of platinum: such as 50 ml, 150 ml, etc.

g) Crucibles of porcelain: such as 50 ml, 150 ml, etc.

h) PTFE/PFA equipment (polytetrafluoroethylene (PTFE)/perfluoro alkoxy alkane resin (PFA): all equipment shall be cleaned with 10 % nitric acid (4.2 c) 2)) before use:

   1) Beakers: such as 100 ml, 200 ml, 500 ml etc.;

   2) Covers for breakers;

   3) Volumetric flasks: such as 100 ml, 200 ml, 500 ml, etc.

i) Micropipettes: such as 10 μl, 100 μl, 200 μl, 500 μl, 1 000 μl etc.

j) Containers: for storage of standard solution and calibrant.

   Containers to be made of high-density polyethylene (PE-HD) or PFA bottles.

k) For determination at the ultra-trace level, containers made of perfluoro alkoxy alkane resin (PFA) or perfluoro (ethylene-propylene) plastic (FEP) shall be used. In either case, the user shall confirm the suitability of the container selected.

l) Electric hot plate or heated sand bath.

m) Muffle furnace: capable of being maintained at 550 °C ± 25 °C.

n) Bunsen burner or similar type of gas burner.

o) Digestion with aqua regia: digestion apparatus equipped with a time and temperature microcontroller unit, a heating block thermostat, a set of vessels, each equipped with reflux coolers and absorption vessels.

p) Microwave digestion system equipped with a sample holder and high-pressure polytetrafluoroethylene/tetrafluoroethylene modified (PTFE/TFM) or perfluoro alkoxy alkane resin/tetrafluoroethylene modified (PFA/TFM) or other vessels based on fluorocarbon materials.

   There are many safety and operational recommendations specific to the model and manufacturer of the microwave equipment used in individual laboratories. The analyst is required to consult the specific equipment manual, manufacturer and literature for proper and safe operation of the microwave equipment and vessels.

q) Heat-resistant thermal insulation board.

r) Glass microfibre filter (borosilicate glass), pore size 0,45 μm and a suitable filter cup.

s) Inductively coupled plasma optical atomic emission spectrometer (ICP-OES).

t) Inductively coupled plasma mass spectrometer (ICP-MS).

u) Atomic absorption spectrometer (AAS).

v) Atomic fluorescence spectrometer (AFS).

6 Sampling

6.1 General

The different test methods, which can be used as alternatives according to this International Standard, need different amounts of sample to obtain the required quality of results. Generally it is advisable to start with the highest amount of sample suitable for the chosen procedure.

In the case of electronics, the sample shall first be destroyed mechanically by appropriate means (e.g. grinding, milling, mill cutting) before chemical dissolution of the powder can start. To ensure representative sample taking at this stage, a certain particle size as a function of the starting amount of sample is required (see IEC 62321-2).

It is recommended to analyse aqueous sample solutions directly after sample preparation. If this is not possible, it is highly recommended to stabilize the solutions in an adequate way, and to store the solutions no longer than 180 days at ambient temperature.

6.2 Test portion

6.2.1 Polymers

For acid digestion, weigh 400 mg of sample that has been ground, milled or cut to the nearest 0,1 mg. For the dry ashing method, or for microwave digestion method, weigh 200 mg of sample that has been ground, milled or cut is measured to the nearest 0,1 mg.

6.2.2 Metals

Weigh 1 g of sample to the nearest 0,1 mg and is placed in a glass beaker or a PTFE/PFA beaker (5.2 h) 1)) when using HF (4.2 e)). For AFS, the quantity of the sample measured is 0,2 g.

6.2.3 Electronics

For digestion with aqua regia, weigh 2 g of the ground sample (maximum particle size: 250 μm) to the nearest 0,1 mg level. For microwave digestion method, weigh 200 mg of ground sample (maximum particle size: 250 μm) to the nearest 0,1 mg.

7 Procedure

7.1 Polymers

7.1.1 General

The samples are pre-cut and/or milled to an appropriate size for the method selected according to the procedure described in Clause 6. Depending on the particular method of preparing the test solution, sample amounts may vary, as described in detail in this clause. The test solution may be prepared by dry ashing or by sample digestion with acids such as nitric acid or sulfuric acid. Acid digestion can be carried out in a closed system using a microwave digestion vessel. Depending on the presence of particular elements, the details of the approach to digestion varies – procedures are given in this clause. Information on the presence of these elements may have been gained from previous screening experiments (IEC 62321-3-1). Finally, in the digestion solution obtained, Pb, Cd and Cr are determined by ICP-OES, ICP-MS or by AAS. In the case of AFS, before determination the digestion solution should be treated additionally for Pb and Cd.

7.1.2 Dry ashing method

If the sample does not contain halogen compounds (information may be available from previous screening experiments), the following steps shall be carried out:

a) Measure the sample into a crucible (5.2 g)) mounted in the hole in the heat-resistant thermal insulation board (5.2 q)).

b) Heat the crucible (5.2 g)) gently with the burner (5.2 n)) in a hood for proper ventilation, taking care that the sample does not ignite.

c) When the sample has decomposed to a charred mass, heating is gradually increased until the volatile decomposition products have been substantially expelled and a dry carbonaceous residue remains.

d) Transfer the crucible and its contents to the muffle furnace (5.2 m)) at 550 °C ± 25 °C with the door left slightly open to provide sufficient air to oxidize the carbon.

e) Heating is continued until the carbon is completely oxidized and a clean ash is obtained.

f) Remove the crucible (5.2 g)) and its contents from the furnace (5.2 m)) and allow to cool to ambient temperature. For AFS, see 7.1.2 h).

g) Add 5 ml of nitric acid (4.2 c) 1)), transfer the resulting solution to a 50 ml volumetric flask (5.2 h) 3)) and fill with water (4.2 a)) to the mark. This is the concentrate sample solution. Dilute the concentrate sample solution with water (4.2 a)) to the appropriate concentration level for each measurement apparatus. If an internal standard (4.2 w)) is to be used, it shall be added before filling. For a final volume of 50 ml, add 500 µl of internal standard (4.2 w)) for ICP-OES and for ICP-MS (after a 1:1 000 dilution step) before filling.

h) Transfer the resulting solution to a 100 ml volumetric flask (5.2 h) 3)) and fill with water (4.2 a)) to the mark. Pipet a 2,50 ml portion of the solution to a 100 ml beaker (5.2 e) 2)). Place the beaker on an electric hot plate (5.2 l)). Heat at low temperature until the solution dries completely. Rinse the inside wall of the beaker with some water (4.2 a)), add either 1,0 ml (for determining Cd) or 1,5 ml (for determining Pb) of hydrochloric acid solution (4.2 d) 2)). Heat up slightly to dissolve the salts in the beaker. Cool down the solution to room temperature, and transfer it to a 50 ml volumetric flask (5.2 h) 3)). The solution in the 50 ml flask will be treated in the following steps respectively:

   - For determination of Pb, fill with water (4.2 a)) to the mark and mix well.
   - For determination of Cd, provided the sample is without impurities such as copper, iron, zinc or nickel etc., add 1,0 ml of cobalt solution (4.2 u)) and 5,0 ml of thiourea solution (4.2 s)) to the volumetric flask. If the sample contains those foreign-metal impurities, then substitute 5,0 ml of thiourea solution (4.2 s) by 10,0 ml of masking agent 2 (4.2 t) 2)). Fill with water (4.2 a)) to the mark and mix well.

   If the sample contains significant amounts of halogen compounds (information may be available from previous screening experiments), the following steps shall be carried out:

i) Measure the sample into a crucible (5.2 g)).

j) Add 5 ml to 15 ml of sulfuric acid (4.2 b) 1)) and heat the crucible (5.2 g)) and its contents slowly on a hot plate or sand bath (5.2 l)) until the plastic melts and blackens.

k) After cooling, add 5 ml of nitric acid (4.2 c) 1)) and continue heating until the plastic degrades completely and white fumes are generated.

l) After cooling, the crucible (5.2 g)) is placed in a muffle furnace (5.2 m)) maintained at 550 °C ± 25 °C and the sample is evaporated, dried and ashed until the carbon has been completely incinerated.

m) After ashing, add 5 ml of nitric acid (4.2 c) 1)) and transfer the resulting solution to a 50 ml volumetric flask (5.2 e) 3)) and fill with water (4.2 a)) to the mark. The resulting solution is the concentrate sample solution. Dilute the concentrate sample solution with water (4.2 a)) to the appropriate concentration level for each measurement apparatus. If an internal standard is to be used, it shall be added before filling. For a final volume of 50 ml 500 µl of internal standard (4.2 w)) for ICP-OES and ICP-MS (after a 1:1 000 dilution step) shall be added before filling.

n) Any sample residues shall be separated by a centrifuge or a filter. The residues shall be checked by appropriate measurements (e.g. XRF, alkali fusion method, other acid digestion methods, etc) to confirm the absence of target elements. The instruction for XRF is given in IEC 62321-3-1.

NOTE This method does not apply to fluorocarbons.

7.1.3 Acid digestion method

This method is used to determine Cd and Cr. It is not suitable for determining Pb, because the sulfuric acid can cause a loss of Pb in the sample due to the formation of $PbSO_4$.

a) Measure the sample into a flask (5.2 e) 1)). Add 5 ml of sulfuric acid (4.2 b.1)) and 1 ml of nitric acid (4.2 c) 1)) and heat the flask until the sample ashes and white fumes are generated. After heating is stopped, nitric acid (4.2 c) 1)) is added in small quantities (approximately 0,5 ml) and heating is continued until white fumes are generated. The heating and decomposition with nitric acid (4.2 c) 1)) are repeated until the decomposed solution turns pale yellow.

b) Allow the sample to cool down for several minutes. Add hydrogen peroxide (4.2 k)) in small quantities, several millilitres at a time, and heat the sample until white fumes are generated. After cooling, transfer the solution to a 100 ml volumetric flask (5.2 e) 3)) and filled with water (4.2 a)) to the mark. The resulting solution is the concentrate sample solution. Dilute the concentrate sample solution with water (4.2 a)) to the appropriate concentration level for each measurement apparatus. If an internal standard is to be used, it shall be added before filling. For a final volume of 100 ml, add 1 000 µl of internal standard (4.2 w)) for ICP-OES and ICP-MS (after a 1:1 000 dilution step) before filling.

c) When general digestion is inadequate or when the sample contains significant amounts of Si, Zr, Hf, Ti, Ta, Nb , W (information may be available from previous screening) the following procedures shall be carried out:

   – Measure the sample into a flask. Add 5 ml of sulfuric acid and 1 ml of nitric acid and heat the flask until the sample ashes and white fumes are generated. Heating is stopped, add nitric acid (4.2 c) 1)) in small quantities (approximately 0,5 l, and heat until white fumes are generated. The heating and decomposition with nitric acid (4.2 c) 1)) are repeated until the decomposed solution turns pale yellow.

   – Allow the sample to cool for several minutes. Hydrogen peroxide is added in small quantities, several millilitres at a time, and heat the sample until white fumes are generated. After cooling, transfer the solution to PTFE/PFA beaker (5.2 h) 1). Add 5 ml of HF (4.2 e)) and heat the vessel until white fumes are generated. Add boric acid (4.2 j)) as desired to permit the complexation of fluoride for protection of the quartz plasma torch (if no acid-resistant sample introduction system is available). After cooling, transfer the solution to a 100 ml PTFE/PFA volumetric flask (5.2 h) 3)) and fill with water (4.2 a)) to the mark. The resulting solution is the concentrate sample solution. Dilute the concentrate sample solution with water (4.2 a)) to the appropriate concentration level for each measurement apparatus. If an internal standard is to be used it shall be added before filling. For a final volume of 100 l, add 1 000 µl of internal standard (4.2 w)) for ICP-OES and ICP-MS (after a 1:1 000 dilution step) before filling.

d) Any sample residues shall be separated by a centrifuge or a filter. The residues shall be checked by appropriate measurements (e.g. XRF, alkali fusion method, other acid digestion methods, etc.) to confirm the absence of target elements. The instruction for XRF is given in IEC 62321-3-1.

NOTE This method is not suitable for AFS.

7.1.4 Microwave digestion

a) Measure the sample into a microwave digestion vessel and add 5 ml of nitric acid (4.2 c) 1)). Add hydrogen peroxide (4.2 k)) in small or catalytic quantities (such as 0,1 ml to 1 ml) as desired to support the complete oxidation of organic matter. Cover the vessel with a lid and place it in a microwave digestion apparatus (5.2 p)). Digest in the microwave oven following a decomposition program specified in advance. Cool the sample. For AFS, carry out as 7.1.2 h). For ICP-OES, ICP-MS or AAS, transfer the solution to a 50 ml volumetric flask (5.2 e) 3)), which is then filled with water (4.2 a)) to the mark. The resulting solution is the concentrate sample solution. Dilute the concentrate sample solution with water (4.2 a)) to the appropriate concentration level for each measurement apparatus. If an internal standard is to be used it shall be added before filling. For a final volume of 50 ml, add 500 µl of internal standard (4.2 w)) for ICP-OES, and ICP-MS (after a 1:1 000 dilution step) before filling.

Hydrogen peroxide should only be added when the reactive components of the sample are known. Hydrogen peroxide may react rapidly and violently with easily oxidizable materials and should not be added if the sample contains large quantities of easily oxidizable organic constituents.

b) When decomposition is inadequate or when the sample contains significant amounts of Si, Zr, Hf, Ti, Ta, Nb , W (information may be available from previous screening), the following procedure shall be carried out:

   – Measure the sample into a microwave digestion vessel. Add 5 ml of nitric acid (4.2 c)1)) and 1 ml of HF (4.2 e)). Add hydrogen peroxide (4.2 k)) in small or catalytic quantities (such as 0,1 ml to 1 ml) to support the complete oxidation of organic matter. Cover the vessel with a lid and place it in a microwave digestion apparatus (5.2 p)). The sample is digested in the microwave oven following a decomposition program specified in advance. Add boric acid (4.2 j)) as desired to permit the complexation of fluoride to protect the quartz plasma torch (if no acid-resistant sample introduction system is available). Cool, the sample and transfer the solution to a 50 ml PTFE/PFA volumetric flask (5.2 h) 3)) and fill the flask with water (4.2 a)) to the mark. The resulting solution is the concentrate sample solution. Dilute the concentrate sample solution may be diluted with water (4.2 a)) to the appropriate concentration level for each measurement apparatus. If an internal standard is to be used it shall be added before filling. For a final volume of 50 ml, add 500 µl of internal standard (4.2 w)) for ICP-OES and ICP-MS (after a 1: 1 000 dilution step) before filling.

Hydrogen peroxide should only be added when the reactive components of the sample are known. Hydrogen peroxide may react rapidly and violently with easily oxidizable materials and should not be added when the sample contains large quantities of easily oxidizable organic constituents.

NOTE This method is not suitable for AFS.

c) Any sample residues shall be separated by a centrifuge or a filter. The residues shall be checked by appropriate measurements (e.g. XRF, alkali fusion method, other acid digestion methods, etc) to confirm the absence of target elements. The instruction for XRF is given in IEC 62321-3-1.

7.2 Metals

7.2.1 General

The preparation of a test sample solution as described here does not necessarily cover all metals and their compounds. Generally, the preparation of a solution with hydrochloric acid, nitric acid or a mixture thereof is recommended. For samples that are difficult to dissolve with these acids, perchloric acid, sulfuric acid, etc. shall be added as necessary. It shall be borne in mind that the use of sulfuric acid is critical in the determination of Pb due to the risk of losing some of the target element. Samples shall be dissolved completely without any residues under heating at high temperatures. A sample may also be dissolved by using phosphoric acid.

When dissolving metals or especially mixtures thereof with strong acids, there is always a risk of precipitation (e.g. Pb and Ba with sulfuric acid and Ag with hydrochloric acid. Al may form oxides/oxide-hydrates and the like). Even if these elements are not covered by legislation, there is the risk of loss of the target element due to co-precipitation. For the purposes of this clause, it has to be ensured that no target elements are lost in the test sample solution. Any residues shall be checked either by a different method to determine whether they contain target elements, or after acid dissolution the residues shall be dissolved completely by other dissolution methods (such as alkali fusion or the use of an air-tight pressurized vessel). The residues treated in this way are then combined with the acid-dissolved solution and measured.

If there are sample residues, they are separated by a centrifuge or a filter. The residues shall be checked by appropriate measurements (e.g. XRF, alkali fusion method, other acid digestion methods, etc) to confirm the absence of target elements. The instruction for XRF is given in IEC 62321-3-1.

If there is a large quantity of tin in the presence of silver, i.e. Pb-free solder, the dissolving acid should be hydrochloric acid followed by the addition of 10 ml of hydrogen peroxide until digestion is complete.

7.2.2 Common methods of sample digestion

a) A glass beaker (5.2 e) 2)) containing the sample is covered with a watch glass (5.2 e) 5)). Add 20 ml of mixed acid 1 (4.2 l) 1)) and heat the beaker until the sample has been dissolved. Allow to cool to room temperature, and rinse the underside of the watch glass and inside wall of the beaker with water (4.2 a)). Transfer the solution to a 100 ml volumetric flask (5.2 e) 3)) and fill with water (4.2 a)) to the mark. The resulting solution is the concentrate sample solution. Dilute the concentrate sample solution with water (4.2 a)) to the appropriate concentration level for each measurement apparatus. If necessary, an internal standard solution (4.2 w)), e.g. containing Rh is added before the flask (5.2 e) 3)) is filled with water (4.2 a)). The type of element and its amount depend on the analytical method selected. The particular paths of dilution shall be taken into account in the calculation of the results. Both the dilution and the internal standard addition shall be documented in the test report.

b) In the case of AFS method, before diluting the concentrate sample solution, pipet a 2,50 ml of portion of the solution to a 100 ml beaker (5.2 e) 2)). Place the beaker on an electric hot plate (5.2 l)). Heat at low temperature until the solution dried completely. Rinse the inside wall of the beaker with some water (4.2 a)), add either 1,0 ml (for determining Cd) or 1,5 ml (for determining Pb) of hydrochloric acid solution (4.2 d) 2)). Heat up slightly to dissolve the salts in the beaker. Cool down the solution to room temperature, and then transfer it to a 50 ml volumetric flask (5.2 e) 3)). The solution in the 50 ml flask will be treated in following steps respectively:

   - For determining Pb, add 4,0 ml of masking agent 1 (4.2 t) 1)) to the volumetric flask and fill with water (4.2 a)) to the mark. After mixed, settle for about 30 min, and then filtrate directly with slow filter paper. Leave the filtrates for test.
   - For determining Cd, add 1,0 ml of cobalt solution (4.2 u)) and 5,0 ml of masking agent 2 (4.2 t) 2)) to the volumetric flask, and fill with water (4.2 a)) to the mark. Settle for about 30 min. Leave the solution for test.

7.2.3 Samples containing Zr, Hf, Ti, Ta, Nb or W

A PTFE/PFA beaker (5.2 h) 1)) containing the sample is covered (5.2 h) 2)). 20 ml of mixed acid 2 (4.2 l) 2)) is added and the beaker (5.2 h) 1)) is heated until the sample is dissolved. After cooling to room temperature, the underside of the cover (5.2 h) 2)) and the inside wall of the beaker (5.2 h) 1)) are rinsed with water (4.2 a)), and the cover (5.2 h) 2)) is removed. The solution is transferred to a 100 ml volumetric flask (5.2 h) 3)) and filled with water to the mark. The resulting solution is the concentrate sample solution. The concentrate sample solution is diluted with water (4.2 a)) to the appropriate concentration level for each measurement apparatus. If necessary, an internal standard solution (4.2 w)), e.g. containing Rh, is added before the flask (5.2 h) 3)) is filled with water (4.2 a)) to the mark. As hydrofluoric acid (4.2 e)) is used, the internal standard solution (4.2 w)) shall not contain rare earth elements. The element chosen and its amount depend on the analytical method selected. The particular paths of dilution shall be taken into account in the calculation of the results. Both the dilution and the internal standard addition shall be documented in the test report.

NOTE This method is not suitable for AFS.

7.2.4 Samples containing Sn

A beaker (5.2 e) 2)) containing the sample is covered. 10 ml of mixed acid 3 (4.2 l) 3)) is added in small quantities. After the violent reaction ends, the beaker (5.2 e) 2)) is heated slowly until the sample is completely dissolved. After cooling, the underside of the cover and the inside wall of the beaker (5.2 e) 2)) are rinsed with water (4.2 a)), and the cover is removed. 10 ml of sulfuric acid (4.2 b) 1)) is added and the beaker (5.2 e) 2)) is heated until white fumes of SO_3 are generated. After cooling for several minutes, 20 ml of hydrobromic acid (4.2 j)) are added, and the beaker (5.2 e) 2)) is heated until white fumes become visible. This process is repeated three times. After cooling to room temperature, 10 ml of nitric acid (4.2 c) 1)) is added to dissolve the salts. The solution is transferred to a 100 ml volumetric flask (5.2 e) 3)) which is then filled with water (4.2 a)) to the mark. The resulting solution is the concentrate sample solution. The concentrate sample solution is diluted with water (4.2 a)) to the appropriate concentration level for each measurement apparatus. If necessary, an internal standard solution (4.2 w)), e.g. containing Rh, is added to the flask (4.1 e) 3)) before it is filled with water (4.2 a)). The element chosen and the amount depend on the analytical method selected. The particular paths of dilution shall be taken into account in the calculation of the results. Both the dilution and the addition of the internal standard solution (4.2 w)) shall be documented in the test report.

Alternatively, 1 g of sample is dissolved by the addition of 40 ml of water (4.2 a)), 12 ml of nitric acid (4.2 c) 1)) and 6 ml of freshly prepared fluoroboric acid (4.2 f)) (200 ml of 40 % hydrofluoric acid (4.2 e) with 75 g of boric acid (4.2 j)). A PTFE/PFA beaker (5.2 h) 3)) and a high-density polyethylene or PTFE/PFA volumetric flask (5.2 h) 1)) shall be used.

NOTE This method is not suitable for AFS.

7.3 Electronics

7.3.1 General

The preparation of a test sample solution, as described here, does not necessarily cover all electronics. It is highly likely that after the digestion methods have been carried out solid residues will be present. It has to be ensured (e.g. by using XRF) that there are no target elements in considerable amounts in the residues. If so, they shall be dissolved by different chemical methods and combined with the test sample solution.

The samples for analysis shall be available as ground material of those electronic products described in Clause 6. The powder is either digested with aqua regia or microwave enhanced with HNO_3, HBF_4, H_2O_2, and HCl. The aqua regia digestion procedure is carried out according to ISO 5961. The elements Pb, Cd and Cr are determined either simultaneously in the digestion solution by ICP-OES or by ICP-MS or one element after the other procedures is determined by AAS or AFS.

NOTE If HBF_4 is not available in sufficient purity, HF can be used instead.

7.3.2 Digestion with aqua regia

a) Weigh 2 g of the ground sample (maximum particle size: 250 μm) to the nearest 0,1 mg level into the reaction vessel and 30 ml of mixed acid 3 (4.2 l) 3) are added. The vessel is equipped with a reflux cooler and an absorption vessel containing 10 ml 0,5 mol/l HNO_3 (4.2 c) 2)). A temperature program is then started to digest the samples for 12 h at room temperature and for 2 h at 120 °C. After cooling to room temperature, the contents of the absorption tube are placed in the reaction vessel, the sample is filtered over a 0,45 μm glass microfibre filter (5.2 r)) and the solid residue is washed four times with 15 ml 5 % HCl (4.2 d) 3)). The solution obtained either is transferred to a 250 ml volumetric flask (5.2.e)3)) and filled with 5 % HCl (4.2 d) 3)) to the mark for ICP-OES, ICP-MS and AAS, or is transferred to a 1 000 ml volumetric flask (5.2 e) 3)) and filled with 5 % (m/m) HCl (4.2.d) 3)) to the mark for AFS.

   The resulting solution is the concentrate sample solution. The concentrate sample solution may be diluted with 5 % HCl (4.2 d) 3)) to the appropriate concentration level for each measurement apparatus. If an internal standard is used, it shall be added before filling. For a final volume of 100 ml, an internal standard of 1 000 μl for ICP-OES and for ICP-MS (after a 1:1 000 dilution step) shall be added.

b) In the case of AFS method, before diluting the concentrate sample solution pipet a 2,50 ml of portion of the solution to a 100 ml of beaker (5.2 e) 2)). Place the beaker on an electric hot plate (5.2 l)). Heat at low temperature until the solution dried completely. Rinse the inside wall of the beaker with some water (4.2 a)), add either 1,0 ml (for determining Cd) or 1,5 ml (for determining Pb) of hydrochloric acid solution (4.2 d) 2)). Heat up slightly to dissolve the salts in the beaker. Cool down the solution to room temperature, and then transfer it to a 50 ml volumetric flask (5.2 e) 3)). The solution in the 50 ml flask will be treated in following steps respectively:

- For determining Pb, add 4,0 ml of masking agent 1 (4.2 t) 1)) to the volumetric flask and fill with water (4.2 a)) to the mark. After mixing, let settle for about 30 min, and then filtrate directly with a 0,45 μm glass microfibre filter (5.2 r)). Leave the filtrates for test.
- For determining Cd, add 1,0 ml of cobalt solution (4.2 u)) and 5,0 ml of masking agent 2 (4.2 t) 2)) to the volumetric flask and fill with water (4.2 a)) to the mark. Settle for about 30 min. Leave the solution for test.

If there are sample residues on the filter, they shall be checked by appropriate measurements (e.g. XRF, alkali fusion method, other acid digestion methods, etc.) to confirm the absence of target elements. The instruction for XRF is given in IEC 62321-3-1.

If the laboratory does not have the recommended equipment described above, it may be possible to use a simpler approach if the user can ensure the suitability of his approach. Deviations from the procedure described above have to be evaluated and documented in the test report. Such a simple approach may be based on a procedure as follows: a glass beaker (5.2 e) 2)) containing the sample is covered with a watch glass (5.2 e) 5)). 30 ml of mixed acid 3 (4.2 l) 3)) is added and the beaker (5.2 e) 2)) is heated for 2 h at 120 °C and then allowed to stand for 12 h at room temperature. The underside of the watch glass (5.2 e) 5)) and inside wall of the beaker (5.2 e) 2)) are rinsed with water (4.2 a)), and the watch glass (5.2 e) 5)) is removed. After cooling, the sample is filtered with a 0,45 μm glass microfibre filter (5.2 r)). The residues are rinsed with 5 % HCl (4.2 d) 3)). The solution is transferred to a volumetric flask (5.2 e) 3)) and filled with 5 % HCl (4.2 d) 3)) to the mark. The resulting solution is used for further measurements.

7.3.3 Microwave digestion

a) Weigh 200 mg of ground sample (maximum particle size: 250 μm) to the nearest 0,1 mg level into a PTFE/TFM, a PTFE/PFA or a vessel made from another fluorocarbon material (5.2 h)). 4 ml of HNO_3 (4.2 c) 1)), 2 ml of HBF_4 (4.2 f)), 1 ml of H_2O_2 (4.2 k)) and 1 ml of water (4.2 a)) are added. The vessels are agitated carefully for approximately 10 s before sealing to allow the escape of immediately formed gases. The sample is then digested in a microwave oven (5.2 p)) following a digestion program specified in advance. During the first digestion step (step A), organic components such as polyvinyl chloride and also some of the metal elements are dissolved.

NOTE 1 If HBF_4 is not available in sufficient purity, HF can be used instead.

NOTE 2 HBF_4 and HF are not suitable for AFS. If only HCl, HNO_3 or a mixture thereof and H_2O_2 are used, then this microwave digestion method may be suitable for AFS.

b) The vessel is opened after cooling to room temperature (approximate time required: 1 h), and 4 ml HCl (4.2 d) 1)) are added. After sealing the vessel again, further elements are dissolved with HCl (4.2 d) 1)) during a second microwave-enhanced digestion step (step B). An example of a suitable microwave program (steps A and B) is given in Table A.6.

c) After cooling the vessel to room temperature (approximate time required: 1 h), it is opened and the solution is filtered over a glass microfibre filter (5.2 r)) into a 25 ml flask (5.2 e) 3)), washed and filled to the mark with 5 % HCl (4.2 d) 3)). If there are sample residues on the filter, they shall be checked by appropriate measurements (e.g. XRF, alkali fusion method, other acid digestion methods, etc.) to confirm the absence of target elements. The instruction for XRF is given in IEC 62321-3-1.

The procedure described above gives the minimum requirements for the microwave digestion system. It is highly recommended that the analysis for each sample is duplicated or triplicated in one run.

It is highly recommended that no more than 200 mg of ground sample be weighed into the digestion vessel. Powdered electronic products with mixtures of HNO_3, HBF_4, H_2O_2 and HCl may react rapidly and violently, and form gas (CO_2, NO_x, etc.). This causes an increase in pressure in the closed vessel. With the sudden development of pressure, the safety system of the microwave oven can react and the vessel open. Target elements might be lost and in the worst case an explosion can occur.

Weigh in the same amounts of sample amounts and types of sample when duplicating or triplicating the analysis in one run.

In cases where more than 200 mg of sample is required to obtain a representative portion of the material to be tested, use the following procedure. Divide the sample into portions of approximately equal mass. Weigh each portion into a separate digestion vessel, follow the digestion procedure with each vessel, and combine the digestion solutions obtained.

EXAMPLE For the digestion of a printed wiring board, a minimum sample amount of 1,2 g is needed. Therefore 6 × 200 mg of ground sample should be weighed into six vessels. After cooling at the end of microwave step B, the vessels are opened, the solutions are combined by filtering over a 0,45 μm glass microfibre filter (5.2 r)) into a 100 ml volumetric flask (5.2 e) 3)), washed and the flask is filled to the mark with 5 % (m/m) HCl (4.2 d) 3)).

If there are sample residues on the filter, they shall be checked by appropriate measurements (e.g. XRF, alkali fusion method, other acid digestion methods, etc.) to confirm the absence of target elements. The instruction for XRF is given in IEC 62321-3-1.

7.4 Preparation of reagent blank solution

The procedure is identical to that of sample preparation and is carried out concurrently but without the sample.

8 Calibration

8.1 General

The sample shall be assumed to be of unknown composition, in which case the internal standard method (intensity comparison method) is recommended. If necessary, a standard addition method or matrix match method may be used. If there are no interfering matrix elements or if the composition of the sample is known, the calibration curve method can be applied.

8.2 Preparation of the calibration solution

After gradually diluting each standard element solution, the diluted standard solutions containing 0 μg to 100 μg of each element are transferred to a 100 ml volumetric flask (5.2 e) 3)). Next, add each reagent, and in the case of AFS or the internal standard method, the appropriate amounts of solution for cobalt solution (4.2 u)) and thiourea solution (4.2 s)), or masking agents (4.2 u)), or the internal standard solutions (4.2 w)) to achieve reagent concentrations identical to those present in the sample solution.

The resulting solution is the mixed calibrant solution for ICP-OES, ICP-MS or AAS.

8.3 Development of the calibration curve

The spectrometers are prepared for quantification. Some of the solution obtained as described in 8.2 is nebulized into the argon plasma or the acetylene/air flame in the case of ICP-OES, ICP-MS or AAS. A HF-resistant sample introduction system shall be used when the sample solution contains HF. In the case of AFS, either Pb(II) in the test solution is oxidized into Pb(IV) by potassium ferricyanide and then reacts with KBH_4 and generates volatile hydride PbH_4, or ionic Cd in the test solution reacts with KBH_4 and generates volatile gas. PbH_4 or gaseous Cd then is separated from the liquid and introduced to quartz furnace with carrier gas (Ar) and atomized.

a) ICP-OES

- Readings are determined for the emission intensity of the target elements (and, if required, of the internal standard element). In the calibration curve method, the curve showing the relationship between the emission intensity of the target elements and their concentrations is developed as the calibration curve. In the internal standard method, the curve showing the relationship between intensity ratio and concentration of the target elements with respect to the curve of the internal standard elements is developed as the calibration curve.
- Recommended wavelengths and interfering elements are shown in Tables A.1 and A.2.

b) ICP-MS

- Readings are determined for the mass/charge (m/z) of the target elements (and, if required, of the internal standard element). In the calibration curve method, the curve showing the relationship between the intensities of the m/z of the target elements and their concentration is developed as the calibration curve. In the internal standard method, the curve showing the relationship between intensity ratio and concentration of the target elements with respect to the curve of the internal standard elements is developed as the calibration curve.
- The m/z ratio may be defined on the basis of the data given in Table A.3.

c) AAS

- Readings are determined for the absorbance of the target elements. In the calibration method, the curve showing the relationship between the absorbance of the target elements and concentration is developed as the calibration curve.
- In the standard additions method, the standards are added into the sample solution and the unknown concentration is determined by extrapolation of the additions curve to zero absorbance.
- The wavelengths shall be selected with regard to typical measurement wavelengths for elements given in Table A.4. If there is interference from co-present substances, the standard additions method should be applied.

d) AFS

- For determining Pb, carrier flow 1 (4.2 r) 1)) and oxido – reduction agent (4.2 p)) should be used. For determining Cd, carrier flow 2 (4.2 r) 2)) and reducing agent 1 (4.2 q) 1)) should be used; Readings are determined for the fluorescence intensity of the target elements. In the calibration method, the curve showing the relationship between the fluorescence intensity of the target elements and concentration is developed as the calibration curve.
- In the standard additions method, the standards are added into the sample solution and the unknown concentration is determined by extrapolation of the additions curve to zero absorbance.
- The wavelengths shall be selected with regard to typical measurement wavelengths for elements given in Table A.5.

8.4 Measurement of the sample

Once the calibration curve has been developed, the laboratory reagent blank and the sample solution are measured. If the sample concentration is above the range of the concentration curve, the solution shall be diluted to the range of the calibration curve, ensuring an appropriate acidification of the calibrants and measured once again.

Measurement precision is checked with a standard substance, calibration solution, etc. at regular intervals (such as once every 10 samples). If necessary, a calibration curve is developed again.

In the event that the calibrant result differs from the expected value by more than 20 %, the calibration and all samples in the sequence shall be re-measured.

If the sample is diluted to the range of calibration, it has to be ensured that the acid, internal standard and other regents concentration in the diluted sample solution is adjusted to the standard solution.

9 Calculation

The concentration measured in 8.4 is the concentration of each element in the sample solution. The concentration of each element in the sample is calculated from the equation:

$$c = \frac{\left(A_1 - A_2\right)}{m} \times V$$

where

c is the concentration of Pb, Cd or Cr in the sample, in µg/g;

A_1 is the concentration of Pb, Cd or Cr in the sample solution, in mg/l;

A_2 is the concentration of Pb, Cd or Cr in the laboratory reagent blank in mg/l;

V is the total volume for the sample solution, in ml, which depends on the particular series of dilutions made;

m is the measured quantity of the sample, in g.

10 Precision

When the values of two independent single test results, obtained using the same method on identical test material in the same laboratory by the same operator using the same equipment within a short interval of time, lie within the range of the mean values cited in Table 1 below, the absolute difference between the two test results obtained will not exceed the repeatability limit *r* deduced by statistical analysis on the international interlaboratory study nos. 2 (IIS2) and 4A (IIS 4A) results in more than 5 % of cases.

When the values of two single test results, obtained using the same method on identical test material in different laboratories by different operators using different equipment, lie within the range of the values cited Table 1 below, the absolute difference between the two results will not be greater than the reproducibility limit *R* by statistical analysis on interlaboratory study nos. 3 (IIS2) and 4A (IIS 4A) results in more than 5 % of cases.

Table 1 – Repeatability and reproducibility

Material type	**IIS**	**Technique**	**Element**	**Mean value** mg/kg	***r*** mg/kg	***R*** mg/kg
Polymer	2	AAS	Pb	480,0	21,1	Insufficient data
Polymer	4A		Pb	953,8	22,5	60,4
				98,3	3,5	3,6
Metal	2		Pb	26,2	4,7	10,6
				188,0	11,9	Insufficient data
Electronic	2		Pb	17 050	990	
Polymer	4A		Cd	98,2	4,2	7,3
				138,5	11,1	9,5
Electronic	2		Cd	14.0	7.9	Insufficient data

Material type	**IIS**	**Technique**	**Element**	**Mean value** mg/kg	***r*** mg/kg	***R*** mg/kg
Polymer	4A		Cr	15,2	3,4	7,8
				98,1	9,7	9,9
Polymer	2	AFS	Pb	109,0	10,1	Insufficient data
				17,3	4,3	Insufficient data
				15,6	2,0	2,6
				902,1	36,2	143,4
	4A			15,6	2,00	2,6
				902,1	36,2	143,4
Metal	2			1 016,0	259,6	Insufficient data
Polymer	2		Cd	131,3	26,0	Insufficient data
				21,3	3,2	Insufficient data
	4A			173,6	6,5	18,0
				91,0	7,1	20,5
Polymer	2	ICP-OES	Pb	444,0	25,9	119,4
				426,2	21,3	307,1
				106,8	15,4	19,7
				14,7	5,2	6,7
				94,8	4,5	17,5
				933	57,0	133,4
	4A			16,5	2,4	10,8
				950,8	32,59	114,8
Metal	2		Pb	206,0	7,4	Insufficient data
				988,0	26,4	61,9
				23,0	1,6	3,0
				193,1	16,9	87,9
Electronic	2		Pb	1 6790	739	2097
				22 450	1 293	1 153
				207 483	42 942	74 907
Polymer	4A		Cd	179,3	8,0	15,7
				98,1	4,0	11,8
Electronic	2		Cd	16,5	3,8	13,1
Polymer	4A		Cr	46,1	3,1	10,9
				15,5	3,3	9,8
Polymer	2	ICP-MS	Pb	481,2	35,5	124,6
				462,3	39,8	194,1
				102,3	1,6	Insufficient data
				16,2	8,1	15,4
				103,8	5,1	7,3
				1049	59,9	332,3

Material type	IIS	Technique	Element	Mean value mg/kg	*r* mg/kg	*R* mg/kg
	4A			15,1	0,73	3,3
				949,2	52,8	70,5
Metal	2		Pb	26,5	2,1	15,1
				156,1	10,8	15,5
				922,4	74,5	327,0
				36,7	4,3	Insufficient data
				190,7	18,6	
Electronic	2		Pb	23 633	1060	Insufficient data
				22 220	4167	6707
Polymer	2		Cd	137,3	8,1	Insufficient data
				22,0	0,0	
				10,0	0,6	1,3
				103,7	3,8	33,1
	4A			180,9	7,8	20,1
				94,4	3,6	12,4
Electronic	2		Cd	24,7	1,6	Insufficient data
Polymer	4A		Cr	39,7	8,7	20,0
	4A			14,2	2,1	3,7
NOTE Repeatability and reproducibility data for some techniques and material types are not available due to limited availability of participating laboratories and appropriate samples for international interlaboratory study.						

See Annex B for supporting data.

11 Quality control

11.1 General

Where applicable the quality assurance and control clauses of the individual test method standards shall include control sample requirements regarding testing frequency and acceptance criteria. This clause shall also include method specific quality control concerns regarding the determination of limits of detection (LOD) and limits of quantification (LOQ). Where applicable, the LOD and LOQ shall be consistent with the descriptions in 11.2. Examples of other method specific quality control concerns include requirements regarding Initial calibration verification, method blanks, laboratory control samples (LCS), and so forth are listed in Table 2.

Table 2 – Acceptance criteria of items for the quality control

Items	Concentration mg/kg in test sample	Acceptance criteria
Calibration curve		$R^2 > 0{,}995$
Initial calibration verification	e.g. 1 mg/kg for Pb, Cd or Cr	Recovery: (90 to 110) %
Continuing calibration verification (CCV)	e.g. 1 mg/kg for Pb, Cd or Cr	Recovery: (90 to 110) %
Method blank		< MDL
Laboratory control sample (LCS)	Middle of calibration range	Recovery: (80 to 120) %

Laboratory control sample duplicate	Middle of calibration range	Relative deviation < 20 %

a) Initial calibration verification is performed whenever a calibration curve is established, using a standard from a source different than calibration standard.

b) One method blank should be analysed at once per a batch. A blank matrix which does not contain Pb, Cd or Cr can be used as a method blank sample.

c) One laboratory control sample (LCS) and laboratory sample duplicate per batch, should be analysed by means spiking Pb, Cd or Cr in the blank matrix. Alternatively, a certified reference material containing Pb, Cd or Cr can be tested in duplicate.

d) After every tenth sample run and at the end of each sample set, analyse a continuing calibration verification standard (CCV). The per cent recovery for Pb, Cd or Cr shall be between 90 % and 110 %. If the per cent recovery for Pb, Cd or Cr in the CCV standard falls outside of this range, the CCV standard should be re-analysed within 12 h. If the recovery is still out of range after re-analysis of the CCV standard, the analysis is stopped and maintenance shall be performed on the system to return it to optimal operating conditions. All samples loaded before the last successful CCV standard may be reported, but all samples after the failing CCC standard shall be re-analysed with a new calibration.

11.2 Limits of detection (LOD) and limits of quantification (LOQ)

The following experimental procedure is performed to determine the method detection limit and limit of quantification for Pb, Cd or Cr.

a) Accurately weigh out the appropriate amount of sample known not to contain Pb, Cd or Cr (e.g. certified reference materials) or other compounds that may interfere with the analysis according to the procedure of interest in Clause 7. Place the sample into each vessel. Repeat this step a minimum of 5 times.

b) Spike each of the vessels with 10 μg Pb, Cd or Cr using the standard solution (4.2 v)).

c) Follow the test procedure of interest in Clause 7 through the digestion and spectroscopic measurement.

d) Calculate the concentration of each element (μg/g) as indicated in Clause 9 and determine the per cent recovery of the spiked element for each of the samples:

$$SR = \frac{C \times M}{SA} \times 100$$

where

SR is the rate of recovery in % of the spiked Pb, Cd or Cr;

C is the measured concentration in μg/g;

M is the sample mass in g;

SA is the spike amount (10 μg).

The per cent recovery of element shall be between 70 % and 125 % for each of the samples. If the recovery is outside the limits for any of the replicates, the entire extraction and analysis procedure shall be repeated.

e) The method detection limit is obtained by calculating the standard deviation, *s*, for the replicate (minimum of 6) analyses. The standard deviation is then multiplied by Student's *t* value for the total number of replicates (*n*) for n-1 degrees of freedom. A list of Student's *t* values for 6 to 10 replicates is shown in Table 3.

EXAMPLE For 6 replicates and 6 – 1 = 5 degrees of freedom, the *t* value would be 3,36.

NOTE All analyses used to calculate an MDL should be consecutive.

Table 3 – Method detection limit = $t \times s_{n-1}$

Number of samples	**Student’s t-statistic** 99 % confidence
6	3,36
7	3,14
8	3,00
9	2,90
10	2,82

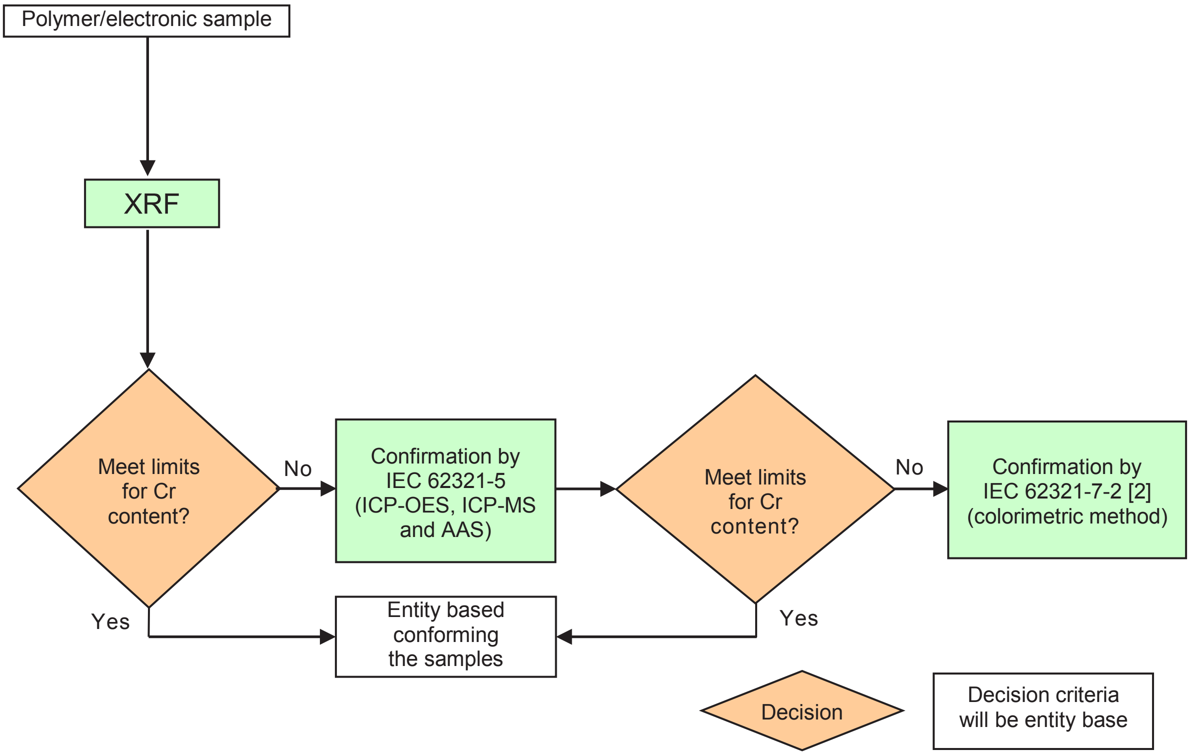
f) The limit of quantification is determined by multiplying the method detection limit by a factor of 5.

Method detection limits and limits of quantification will vary from laboratory to laboratory. Generally, a method detection limit of 2 µg/g (limit of quantification of 10 µg/g) has been found achievable using this method.

Annex A
(informative)

Practical application of determination of Cd , Pb and Cr in polymers and electronics and Cd and Pb in metals by AAS, AFS, ICP-OES and ICP-MS

A.1 Flow chart for Cr analysis



A.2 ICP-OES

Table A.1 – Spectral interferences for the wavelengths of Cd and Pb *(1 of 2)*

Element	**Cd**	**Cd**	**Cd**	**Cd**	**Pb**	**Pb**	**Pb**	**Pb**
nm	**214,439**	**226,502**	**228,802**	**361,051**	**217,000**	**220,353**	**261,417**	**283,305**
Ag	+	+	+	+	+	+	+	+
As	++	+	+++	+	+	+	+	+
Au	+	+	++	+	+	+	+	+++
B	+	+	+	+++	+	+	++	+
Ca	+	+	+	+	+	+	+	+
Co	+	++	+++	+++	++	+++	+++	++
Cr	+	+	+	+	+	+	++	+
Cu	+	+	+	+	+	+	+	++
Eu	+	+	+	+++	++	+	+++	+++
Ga	+	+	+	+	+	+	+	+
Ge	+	+	+	+	+	+	+	+
In	+	+	+	+	+	+	+	+
Ir	++	++	++	++	+++	+++	+++	+++
Mg	+	+	+	+	+	+	+	++
Mn	+	+	+	+++	+	++	+++	+
Mo	++	+	+	+++	++	+	++	+++
Ni	+	+	++	+++	+++	++	+	+
Pd	+	+	+	+	+	+++	+	+
Pt	+++	+	++	+	+	+	+	+
Re	++	++	+	+++	++	+++	++	+++
Ru	++	+	++	+	++	+	+++	+
Sb	++	+	+	+	++	+	+	+
Sc	+	+	+++	++	++	++	+++	++
Sn	+	+	+	+	++	+	+	++
V	+	+	++	+++	++	++	++	+
W	++	++	++	++	+++	+	+++	++
Zn	+	+	+	+	+++	+	+	+
Al	+	+	+	+	+++	+++	+	++
Ti	+	+	+	++	+	+++	+	++
Fe	+++	+++	+	++	+++	++	+++	+++
Nb	+	+	+	–	–	+	–	+++
Hf	–	–	–	–	–	+	–	+++

Table A.1 *(2 of 2)*

Element	**Cd**	**Cd**	**Cd**	**Cd**	**Pb**	**Pb**	**Pb**	**Pb**
nm	**214,439**	**226,502**	**228,802**	**361,051**	**217,000**	**220,353**	**261,417**	**283,305**
Ta	–	–	–	–	–	+	–	++
Pb	+	+	+	+	–	–	–	–
Cd	–	–	–	–	+	+	+	+

NOTE Table A.1 shows the strength of interference for the wavelengths of Cd and Pb when 1 000 mg/kg of the corresponding matrix elements are introduced.

+ No or small interference (typically less than 0,05 mg/kg).
++ Medium interference (typically between 0,05 mg/kg and 0,2 mg/kg).
+++ Strong interference (typically more than 0,2 mg/kg).

Table A.2 – Spectral interferences for the wavelengths of Cr

Element	**Cr**	**Cr**	**Cr**	**Cr**	**Cr**	**Cr**
nm	**205,560**	**206,158**	**267,716**	**283,563**	**284,325**	**357,869**
Ag	–	–	–	–	+	–
As	–	–	–	–	–	–
Au	–	–	–	+	–	–
B	–	–	–	–	–	–
Ca	–	–	–	–	–	+
Co	–	–	–	–	–	+
Cr	–	+	–	+	+	–
Cu	-	–	-	–	–	–
Eu	–	–	–	–	–	–
Ga	–	–	–	–	–	–
Ge	–	–	–	–	–	–
In	–	–	–	+	–	–
Ir	+	+	-	+	–	–
Mg	–	–	–	–	–	–
Mn	–	–	+	–	–	–
Mo	+	–	+	++	++	+
Ni	+	+	–	–	–	–
Pd	–	–	–	–	–	–
Pt	–	+	+	–	–	–
Re	–	–	–	–	+	+
Ru	–	–	+	+	+	–
Sb	–	++	–	–	–	–
Sc	–	–	–	–	–	–
Sn	–	–	–	–	–	–
V	+	+	+	+	+	+
W	–	+	++	+	+	–
Zn	–	+	–	–	–	–
Al	–	+	–	–	–	–

Element	Cr	Cr	Cr	Cr	Cr	Cr
Ti	–	–	–	+	–	+
Fe	–	–	+	++	++	–
Nb	–	+	++	+	++	+
Hf	–	+	++	+	–	–
Ta	–	+	-	+	++	–
Pb	–	+	–	–	–	–
Cd	–	–	+	–	–	–
NOTE Table A.2 shows the strength of interference for the wavelengths of Cd and Pb when 1 000 mg/kg of the corresponding matrix elements are introduced.						
+ No or small interference (typically less than 0,05 mg/kg). ++ Medium interference (typically between 0,05 mg/kg and 0,2 mg/kg). +++ Strong interference (typically more than 0,2 mg/kg).						

A.3 ICP-MS

If a stable isotope is found, the mass/charge (m/z) number of several isotopes can be measured to estimate the level of spectral interference). This is illustrated in Table A.3. If the sample contains tin or molybdenum, attention shall be paid to positive interference in Cd mass measurement.

Table A.3 – Examples of mass/charge (m/z) ratios

Element	Isotope	Isobar	Polyatomic ion
Cd	$_{111}$Cd		MoO, MoOH, ZrOH
	$_{112}$Cd	Sn	MoO, MoOH
	$_{113}$Cd	In	MoO, MoOH, ZrOH, RuO
	$_{114}$Cd	Sn	MoO, MoOH, RuO
Pb	$_{204}$Pb		
	$_{206}$Pb		PtO
	$_{207}$Pb		IrO
	$_{208}$Pb		PtO
Cr	$_{52}$Cr		SO, ClO, HClO, ArC, ArN, ArO
	$_{53}$Cr		HSO, ClO, HClO, ArC

A.4 AAS

Recommended measurement wavelengths for AAS are shown in Table A.4.

Table A.4 – Examples of wavelengths for AAS

Element	Wavelength nm	Slit width nm
Cd	228,8	0,7
Pb	261,4	0,7
	217,0	0,7
	283,3	0,7
Cr	357,9	0.7

Light source: electrodeless discharge lamp or hollow cathode lamp, gas type: acetylene/air.

A.5 AFS

Recommended measurement wavelengths for AFS are shown in Table A.5.

Table A.5 – Examples of wavelengths for AFS

Element	Wavelength nm
Cd	228,8
Pb	283,3

Light source: electrodeless discharge lamp or hollow cathode lamp, gas type: argon.

A.6 Background correction

In the event of changing background by the main matrix of the solution which affects the emission intensities (Ix), these emission intensities shall be obtained by deducting the background intensities (Ix'). Figure A.1 shows an example of the effect of background correction. Figure A.1a shows an example of uniform background versus wavelength. In this case, the background could be corrected by both positions A and B. Figure A.1b shows an example of changing background versus wavelength. In this case, background intensities shall be corrected by obtaining the background intensities (Ix'), which are calculated by both position A and position B of the emission intensities.

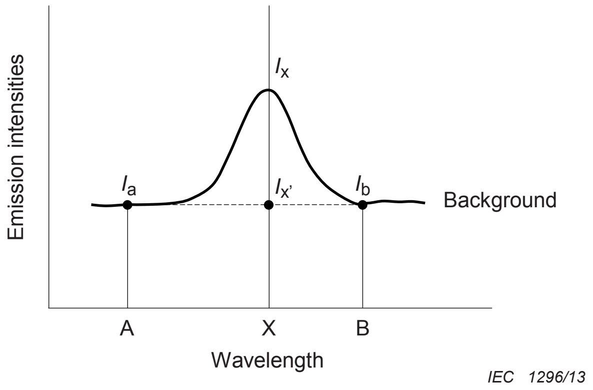


Figure A.1a – Uniform background versus wavelength

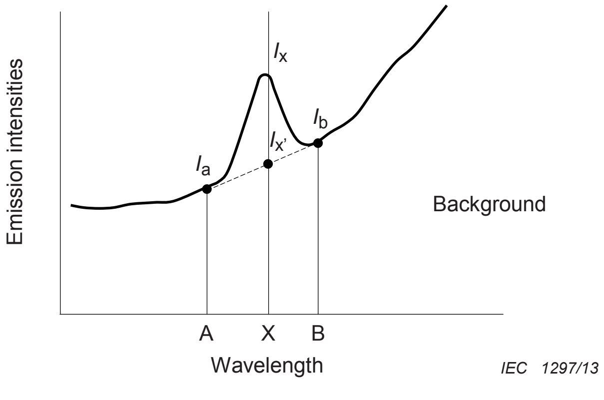


Figure A.1b – Changing background versus wavelength

Figure A.1 – Background correction

When using a standard addition method, the background shall be subtracted by the above background correction method before a standard addition calibration can be made.

A.7 Program for microwave digestion

Table A.6 provides an example of program for microwave digestion of samples.

Table A.6 – Program for microwave digestion of samples[a]

Step	**Time** min	**Power output** W	**Pressure limited to** MPa
1A	5	300	2,5
2A	5	350	2,5
3A	17	450	2,5
4A	2	300	2,5
Ventilation step A	3	0	2,5
1B	5	300	2,5
2B	5	400	2,5
3B	17	450	2,5
Ventilation step B	3	0	2,5

[a] Power output for five vessels.

Annex B
(informative)

Results of international interlaboratory study nos. 2 (IIS2) and 4A (IIS 4A)

Table B.1 – Statistical data for AAS[3]

Polymer sample	**Parameter**	***m*** mg/kg	***v*** mg/kg	***n***	***s***(***r***) mg/kg	***r*** mg/kg	***s***(***R***) mg/kg	***R*** mg/kg
IIS2-B09	Pb	480,0	380-640	3	7,5	21,1	Insufficient data	
IIS4A-05	Pb	953,8	954,3	10	8,04	22,51	21,56	60,37
IIS4A-08	Pb	98,3	98	10	1,26	3,54	1,29	3,60
IIS4A-05	Cd	98,2	100	10	1,50	4,20	2,619	7,333
IIS4A-08	Cd	138,5	137	10	3,98	11,14	3,39	9,49
IIS4A-05	Cr	15,2	16	10	1,21	3,38	2,78	7,79
IIS4A-08	Cr	98,1	100	9	3,45	9,67	3,54	9,92
Metal sample								
IIS2-D17	Pb	26,2	30	6	1,7	4,7	3,8	10,6
IIS2-D15	Pb	188,0	190	2	4,2	11,9	Insufficient data	
Electronic sample								
IIS2-F20	Cd	14,0	20	2	2,8	7,9	Insufficient data	
IIS2-F20	Pb	17050	23 000	2	354	990	Insufficient data	

Table B.2 – Statistical data for AFS

Polymer sample	**Parameter**	***m*** mg/kg	***v*** mg/kg	***n***	***s***(***r***) mg/kg	***r*** mg/kg	***s***(***R***) mg/kg	***R*** mg/kg
IIS2-C10	Pb	109,0	107,6	3	3,6	10,1	Insufficient data	
IIS2-C11	Pb	17,3	13,8	3	1,5	4,3		
IIS4A-04	Pb	15,6	15,7	18	0,71	1,98	0,94	2,63
IIS4A-05	Pb	902,1	954	18	12,93	36,21	51,21	143,38
IIS2-C10	Cd	131,3	140,8	3	9,3	26,0	Insufficient data	
IIS2-C11	Cd	21,3	21,7	3	1,2	3,2		
IIS4A-04	Cd	173,6	183	18	2,33	6,53	6,44	18,02
IIS4A-05	Cd	91,0	100	18	2,53	7,08	7,33	20,51
Metal sample								
IIS2-D16	Pb	1016,0	930	3	92,7	259,6	Insufficient data	

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[3] An explanation for the symbols in the column header for Tables B.1, B.2, B.3 and B.4 is given in Table B.4.

Table B.3 – Statistical data for ICP-OES

Polymer sample	**Parameter**	***m*** mg/kg	***v*** mg/kg	***n***	***s*(*r*)** mg/kg	***r*** mg/kg	***s*(*R*)** mg/kg	***R*** mg/kg
IIS2-B08	Pb	444,0	390-665	9	9,3	25,9	42,6	119,4
IIS2-B09	Pb	426,2	380-640	9	7,6	21,3	109,7	307,1
IIS2-C10	Pb	106,8	107,6	25	5,5	15,4	7,0	19,7
IIS-C11	Pb	14,7	13,8	23	1,9	5,2	2,4	6,7
IIS2-C12	Pb	94,8	108,9	12	1,6	4,5	6,3	17,5
IIS-C13	Pb	933	1084	12	20,4	57,0	47,6	133,4
IIS4A-04	Pb	16,5	15,70	21	0,85	2,37	3,87	10,84
IIS4A-05	Pb	950,8	954	24	11,64	32,59	40,99	114,78
IIS2-C10	Cd	142,4	140,8	23	2,6	7,3	3,9	11,0
IIS2-C11	Cd	20,9	21,7	28	1,5	4,3	2,6	7,3
IIS2-C12	Cd	9,7	10,8	12	0,6	1,5	0,7	2,0
IIS2-C13	Cd	95,8	106,9	12	2,7	7,5	6,6	18,5
IIS4A-04	Cd	179,3	183	27	2,84	7,96	5,62	15,73
IIS4A-05	Cd	98,1	100	24	1,43	4,00	4,22	11,82
IIS4A-04	Cr	46,1	47	18	1,11	3,10	3,89	10,90
IIS4A-05	Cr	15,5	16	21	1,18	3,29	3,52	9,84
Metal sample								
IIS2-D18	Pb	206,0	174	3	2,6	7,4	Insufficient data	
IIS2-D16	Pb	988,0	930	6	9,4	26,4	22,1	61,9
IIS2-D17	Pb	23,0	30	6	0,6	1,6	1,1	3,0
IIS2-D15	Pb	193,1	190	11	6,0	16,9	31,4	87,9
Electronic sample								
IIS2-F20	Cd	16,5	20	11	1,3	3,8	4,7	13,1
IIS2-F20	Pb	16 790	23 000	11	264	739	749	2 097
IIS2-F21	Pb	22 450	22 000	6	462	1293	412	1 153
IIS2-F22	Pb	207 483	222 534	12	15 336	42 942	26 752	74 907

Table B.4 – Statistical data for ICP-MS

Polymer sample	**Parameter**	***m*** [a] mg/kg	***v*** [b] mg/kg	***n*** [c]	***s*(*r*)** [d] mg/kg	***r*** [e] mg/kg	***s*(*R*)** [f] mg/kg	***R*** [g] mg/kg
IIS2-B08	Pb	481,2	390-665	12	12,7	35,5	44,5	124,6
IIS2-B09	Pb	462,3	380-640	6	14,2	39,8	69,3	194,1
IIS2-C10	Pb	102,3	107,6	3	0,6	1,6	Insufficient data	
IIS-C11	Pb	16,2	13,8	6	2,9	8,1	5,5	15,4
IIS2-C12	Pb	103,8	108,9	6	1,8	5,1	2,6	7,3
IIS-C13	Pb	1049	1084	6	21,4	59,9	118,7	332,3
IIS4A-04	Pb	15,1	15,7	15	0,26	0,73	1,17	3,28
IIS4A-05	Pb	949,2	954	15	18,84	52,75	25,19	70,52
IIS2-C10	Cd	137,3	140,8	3	2,9	8,1	Insufficient data	
IIS2-C11	Cd	22,0	21,7	3	0,0	0,0		
IIS2-C12	Cd	10,0	10,8	6	0,2	0,6	0,5	1,3
IIS-C13	Cd	103,7	106,9	6	1,4	3,8	11,8	33,1
IIS4A-04	Cd	180,9	183	12	2,78	7,79	7,19	20,14
IIS4A-05	Cd	94,4	100	15	1,27	3,55	4,44	12,43
IIS4A-04	Cr	39,7	47	15	3,10	8,69	7,16	20,04
IIS4A-05	Cr	14,2	16	15	0,75	2,09	1,32	3,69
Metal sample								
IIS2-D14	Pb	26,5	30	9	0,7	2,1	5,4	15,1
IIS2-D18	Pb	156,1	174	9	3,9	10,8	5,5	15,5
IIS2-D16	Pb	922,4	930	12	26,6	74,5	116,8	327,0
IIS2-D17	Pb	36,7	30	3	1,5	4,3	Insufficient data	
IIS2-D15	Pb	190,7	190	3	6,7	18,6		
Electronic sample								
IIS2-F20	Cd	24,7	20	3	0,6	1,6	Insufficient data	
IIS2-F20	Pb	23 633	23 000	3	379	1060		
IIS2-F21	Pb	22 220	22 000	12	1488	4167	2 395	6 707

[a] *m* is the arithmetic mean of test results.

[b] *v* is the expected value.

[c] *n* is the number of accepted results.

[d] *s*(*r*) is the repeatability standard deviation.

[e] *r* is the repeatability limit.

[f] *s*(*R*) is the reproducibility standard deviation.

[g] *R* is the reproducibility limit.

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ASTM E 353-93, *Standard test methods for chemical analysis of stainless, heat resisting, maraging, and other similar chromium-nickel-iron alloys*

ASTM E 363-93, *Standard methods for chemical analysis of chromium and ferrochromium*

ASTM E 361-99, *Standard test methods for the determination of arsenic and lead in ferromanganese*

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