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Electrotechnical products – Determination of levels of six regulated substances (lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls, polybrominated diphenyl ethers)

Produits électrotechniques – Détermination des niveaux de six substances réglementées (plomb, mercure, cadmium, chrome hexavalent, diphényles polybromés, diphényléthers polybromés)

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CONTENTS

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ELECTROTECHNICAL PRODUCTS – DETERMINATION OF LEVELS OF SIX REGULATED SUBSTANCES (LEAD, MERCURY, CADMIUM, HEXAVALENT CHROMIUM, POLYBROMINATED BIPHENYLS, POLYBROMINATED DIPHENYL ETHERS)

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International Standard IEC 62321 has been prepared by IEC technical committee 111: Environmental standardization for electrical and electronic products and systems.

The text of this standard is based on the following documents:

FDIS	Report on voting
111/116/FDIS	111/125/RVD

Full information on the voting for the approval of this standard can be found in the report on voting indicated in the above table.

This publication has been drafted in accordance with ISO/IEC Directives, Part 2.

The committee has decided that the contents of this publication will remain unchanged until the maintenance result date indicated on the IEC web site under "http://webstore.iec.ch" in the data related to the specific publication. At this date, the publication will be

- reconfirmed,
- withdrawn,
- replaced by a revised edition, or
- amended.

INTRODUCTION

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

The use of certain substances such as lead (Pb), mercury (Hg), cadmium (Cd), hexavalent chromium (Cr(VI)) contained in inorganic and organic compounds, and two types of brominated flame retardants, polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE) in electrotechnical products, is regulated in current and proposed regional legislation.

The purpose of IEC 62321 is therefore to provide test methods that will allow the electrotechnical industry to determine the levels of regulated substances Pb, Hg, Cd, Cr(VI) and their compounds, as well as PBB and PBDE in electrotechnical products on a consistent global basis.

ELECTROTECHNICAL PRODUCTS – DETERMINATION OF LEVELS OF SIX REGULATED SUBSTANCES (LEAD, MERCURY, CADMIUM, HEXAVALENT CHROMIUM, POLYBROMINATED BIPHENYLS, POLYBROMINATED DIPHENYL ETHERS)

1 Scope

IEC 62321, which is an International Standard, specifies the determination of the levels of lead (Pb), mercury (Hg), cadmium (Cd), hexavalent chromium (Cr(VI)) contained in inorganic and organic compounds, and two types of brominated flame retardants, polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE) contained in electrotechnical products.

This standard refers to the sample as the object to be processed and measured. The nature of the sample and the manner in which it is acquired is defined by the entity carrying out the tests and not by this standard.

NOTE 1 Further guidance on obtaining representative samples from finished electronic products to be tested for levels of regulated substances may be found in the future IEC Publicly Available Specification (PAS) for sampling disjointment[1].

It is noted that the selection of the sample may affect the interpretation of the test results.

This standard does not determine:

- the definition of a “unit” or “homogenous material” as the sample;
- the disassembly procedure employed for obtaining a sample;
- assessment procedures.

NOTE 2 Further guidance on assessment procedures may be found in the future IEC Technical Specification IEC/TS 62476[1][2].

2 Normative references

The following referenced documents are indispensable for the application 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/IEC Guide 98:1995, *ISO Guide to the expression of uncertainty in measurement (GUM*)

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

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

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

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1 Under consideration, no number yet assigned.

2 Figures in square brackets refer to the bibliography.

3 Terms, definitions and abbreviations

3.1 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1.1
analyte
substance to be measured

3.1.2
calibrant
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 blank
substance identical in form and matrix composition to the calibrant(s) but containing no analyte(s)

3.1.4
certified reference material
CRM
reference material, accompanied by a certificate, one or more of whose properties are certified by a procedure which establishes traceability to an accurate realization of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence

[ISO Guide 30][2]

3.1.5
digestate
solution obtained after completion of sample digestion process

3.1.6
electronic assembly
group of components, at least one of which is an electronic device, but in which individual parts may be replaced without damage to the assembly

EXAMPLE Group of components mounted on a printed wiring board.

[IEC 60730-1:1999, definition H.2.5.9][3]

3.1.7
electronic components
electrical or electronic devices that are not subject to disassembly without destruction or impairment of design use. They are sometimes called electronic parts, or piece parts

EXAMPLES Resistors, capacitors, diodes, integrated circuits, hybrids, application-specific integrated circuits, wound components and relays.

[IEC/TS 62239:2003][4]

3.1.8
electronics
electronic assembly and/or electronic component and/or field-replaceable unit

3.1.9
field replaceable unit
FRU
part, component or subassembly that is easily removed (mechanically disjointed) using ordinary tools

NOTE "Easily removed" means using ordinary tools to perform such functions as screwing or disconnecting, and only without irreversibly destroying the unit.

[IEC Guide 114:2005, definition 3.7][5]

3.1.10
matrix
material or substance and its form or state in which analyte is embedded or to which analyte is attached

3.1.11
performance-based measurement system
PBMS
set of processes wherein the data needs, mandates or limitations of a program or project are specified, serving as criteria for selecting appropriate methods to meet those needs in a cost-effective manner

NOTE The criteria may be published in regulations, technical guidance documents, permits, work plans or enforcement orders.

3.1.12
reference material
material or substance, one or more of whose property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method or for assigning values to materials

[ISO Guide 30, modified]

3.2 Abbreviations

AAS	Atomic absorption spectrometry
ABS	Acrylonitrile butadiene styrene
AFS	Atomic fluorescence spectrometry
ASTM	American Society for Testing and Materials
BCR	Community Bureau of Reference (BCR : *Bureau Communautaire de Référence*)
BL	Below limit
BSA	N,O-bis(trimethylsilyl) acetamide
BSTFA	N,O-bis(trimethylsilyl)-trifluoroacetamide
CCC	Continuing calibration check standard
CCFL	Cold cathode fluorescent lamp
CFR	Code of Federal Regulations
CRM	Certified reference material
CV-AAS	Cold vapour atomic absorption spectrometry
CV-AFS	Cold vapour atomic fluorescence spectrometry
DBOFB	4,4'-dibromooctafluorobiphenyl
DIN	Deutsches Institut für Normung
DMDCS	Dimethyldichlorosilane in dichloromethane
EC	European Community

EDXRF	Energy dispersive X-ray fluorescence
EI	Electron ionization
EN	European norm
EPA	Environmental Protection Agency
EVAC	Ethylene vinyl acetate
FEP	Perfluoro(ethylene-propylene)
FP	Fundamental parameters
FRU	Field replaceable unit
GC	Gas chromatography
GC-MS	Gas chromatography – mass spectrometry
GLP	Good laboratory practice
HPLC-UV	High-performance liquid chromatography – ultraviolet
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
IS	Internal standard
IIS	International interlaboratory study
IUPAC	International Union of Pure and Applied Chemistry
JIS	Japanese Industrial Standard
LN	Liquid nitrogen
LOD	Limit of detection
LOQ	Limit of quantification
MDL	Method detection limit
NIST	National Institute of Standards and Technology
NMIJ	National Metrology Institute of Japan
OctaBB	Octabromobiphenyl
OctaBDE	Octabromodiphenyl ether
OL	Over limit
PAS	Publicly Available Specification
PBB	Polybrominated biphenyl
PBDE	Polybrominated diphenyl ether
PBMS	Performance-based measurement system
PC	Polycarbonate
PE	Polyethylene
PE-HD	High-density polyethylene
PFA	Perfluoro alkoxyl alkane resin
PS-HI	High-impact polystyrene
PTFE	Polytetrafluoroethylene
PTV	Programmable temperature vaporization
PVC	Polyvinyl chloride
PWB	Printed wiring board
QA	Quality assurance
QC	Quality control
RH	Relative humidity

RSD	Relative standard deviation
SIM	Single (or “selected”) ion monitoring
SOP	Standard Operating Procedure
SRM	Standard reference material
TFM	Tetrafluoroethylene modified
US	United States
WC	Tungsten carbide
WDXRF	Wavelength dispersive X-ray fluorescence
XRF	X-ray fluorescence

4 Test methods – Overview

4.1 Field of application

The contents of the test methods to determine the levels of regulated substances are grouped in two important steps:

- Analytical test methods
- Laboratory implementation

Analytical test methods were developed and validated to ensure their suitability to the task. They are divided into five main parts:

- Overview
- Apparatus/equipment and materials
- Reagents
- Sample preparation
- Test method, which includes:
  - calibration;
  - instrument performance;
  - sample analysis;
  - calculation of analytical results;
  - test report;
  - quality control.

Descriptions of individual test methods follow this outline.

Laboratory implementation is not covered in this standard, as laboratories are able to implement test methods described using test methods and standards addressed in other sources. The implementation step includes suitable quality assurance measures and a validation protocol that documents the performance of the analytical method using the instruments in the laboratory. Quality assurance systems such as good laboratory practice (GLP) and/or accreditation to similar international or national systems (e.g. ISO 17025) are strongly encouraged.

4.2 Sample

This standard refers to the sample as the object to be processed and measured according to the test methods to determine the levels of the regulated substances. A sample can either be a polymer, a metal or electronics.

What the sample is or how to get to the sample shall be defined with respect to applicable normative documents by the entity carrying out the test methods.

NOTE The entity can be either the organization commissioning the work or the organization carrying out the work. In practice the requestor and the analyst will probably agree on the sample to be taken.

The entity may decide to prepare a sample that is a homogenous material. For this kind of sample, the test methods applicable to metals or polymers are especially suitable.

The entity may also decide to prepare a sample which is an electronic component, an electronic assembly or a field replaceable unit (FRU). For this kind of sample, the test methods applicable to electronics are especially suitable.

The methods to obtain the sample are outside the scope of this standard. Further guidance may be found in the future IEC Publicly Available Specification (PAS) for sample disjointment.

4.3 Test methods – Flow chart

Figure 1 gives a flow chart of the test methods to determine the levels of regulated substances in electrotechnical products.

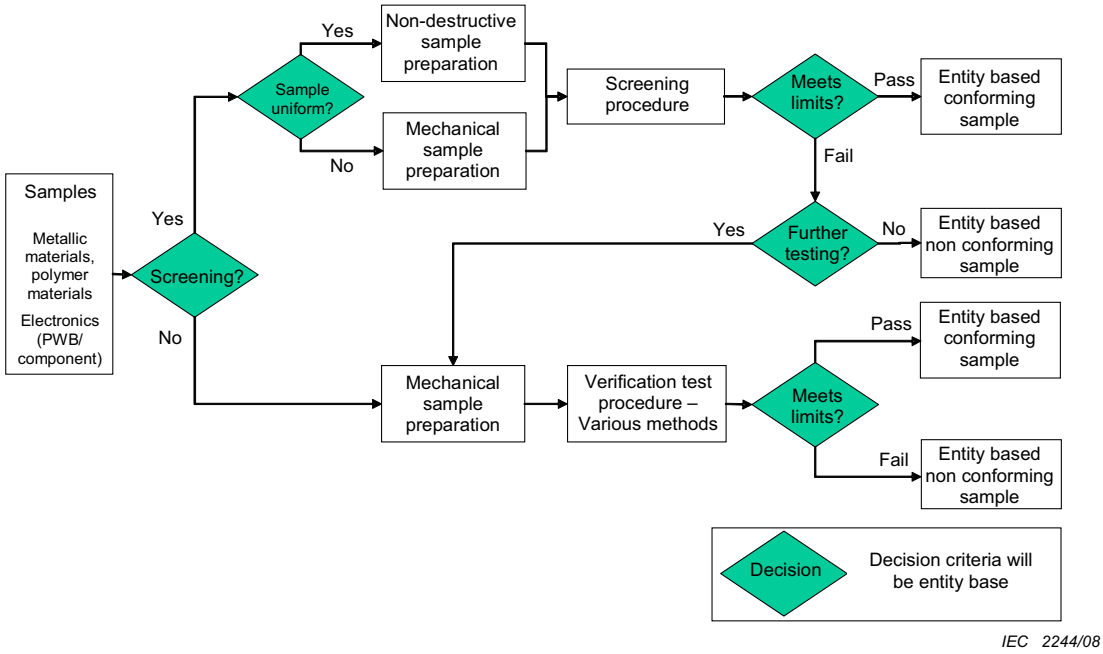

Figure 1 – Flow chart of the test methods

After obtaining the sample, which is either a polymer, a metal or electronics (e.g. in the form of electronic components, electronic assemblies or FRUs), a decision is taken as to whether the screening procedure or the verification procedure using a variety of test methods will be used.

The screening procedure may be carried out either by directly measuring the sample (non-destructive sample preparation) or by destroying the sample to make it uniform (mechanical sample preparation). This decision shall be made by judging the uniformity of the sample. A screening of representative samples of many uniform materials (such as polymers, alloys, glass) may be done non-destructively, while for other more complex samples (such as a FRU), mechanical sample preparation may be an appropriate solution. Mechanical sample preparation is the same for both the screening and the verification test procedure. The procedure for mechanical sample preparation is described in Clause 5.

A sample is screened using any XRF spectrometer (e.g. EDXRF (energy dispersive X-ray fluorescence) or WDXRF (wavelength dispersive X-ray fluorescence) spectrometer, providing it has the performance characteristics described in Clause 6. The screening procedure shall be performed under controlled conditions. There are limitations on the use of the XRF analysis technique and the applicability of the results obtained, although its speed and resource efficiency has its merits, particularly in meeting the demands of the electrotechnical industry.

The verification procedure is performed after mechanical sample preparation using a variety of test methods tailored to the regulated substances and the sample, which can be a polymer, a metal or electronics. Table 1 gives an overview of the verification methods, which are described in detail in Clauses 7 to 10 and in Annexes A, B and C. The purpose of using a particular verification test method is to ensure the most accurate results possible, although it will most likely require more resources to carry out.

Table 1 – Overview of the content of the verification procedure

Steps	Substances	Polymers	Metals	Electronics (PWBs/components)
Mechanical sample preparation (see Clause 5)		Direct measurement Grinding	Direct measurement Grinding	Grinding
Chemical sample preparation		Microwave digestion Acid digestion Dry ashing Solvent extraction	Microwave digestion Acid digestion	Microwave digestion Acid digestion Solvent extraction
Analytical technique definition (including typical margins of error)	PBB/PBDE	GC-MS (see Annex A)	NA	GC-MS (see Annex A)
	Cr(VI)	Alkaline digestion/ colorimetric method (see Annex C)	Spot-test procedure/ boiling water extraction procedure (see Annex B)	Alkaline digestion/ colorimetric method (see Annex C)
	Hg	CV-AAS, CV-AFS, ICP-OES, ICP-MS (see Clause 7)		
	Pb/Cd	ICP-OES, ICP-MS, AAS (see Clause 8)	ICP-OES, ICP-MS, AAS (see Clause 9)	ICP-OES, ICP-MS, AAS (see Clause 10)

After the verification procedure has been carried out, it shall be decided whether the sample meets the limits based on the entity's criteria for regulated substances.

4.4 Adjustment to the matrix

Test methods for regulated substances that are present at relatively low levels amongst other chemical elements or compounds at relatively high concentrations, or those that represent the major constituent of the sample, are very often material or matrix dependent. Therefore the test methods shall be adjusted to the materials to be tested, either by introducing the appropriate blanks and matrix-adjusted calibration samples, or by a preparation step that separates the analyte from the adherent materials or the main matrix. The main material types (or matrices) in electronic equipment are polymers (mostly technical polymers containing additives and sometimes having coated surfaces), metals or alloys (they may also be coated) and electronics.

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

In its simplest form, a limit of detection (LOD) or method detection limit (MDL) is typically described as the lowest amount or concentration of analyte in a test sample that can be reliably differentiated from zero for a given measurement system.

Instrument detection limits represent an instrument's ability to differentiate low concentrations of analytes from "zero" in a blank or standard solution, and are commonly used by manufacturers to demonstrate the measurement capability of a system (e.g. atomic absorption spectrometer). Whilst instrument detection limits are useful, they are often considerably lower than a limit of detection representing a complete analytical method measurement process.

Complete analytical method detection limits are most appropriately determined experimentally by performing replicate, independent measurements on low-level or fortified sample matrices (e.g. plastic) carried out through the entire test procedure, including sample digestion or extraction. A minimum of six replicates and analyte concentrations of 3 to 5 times the estimated method detection limit have been suggested as suitable for this analysis. The complete method detection limit for an entire test procedure is determined by multiplying the standard deviation of the replicates by an appropriate factor. The International Union of Pure and Applied Chemistry (IUPAC) recommends a factor of 3 for a minimum of six replicates, while the United States Environmental Protection Agency (US EPA) utilizes a one-sided confidence interval with the multiplier equal to Student's t value chosen for the number of replicates and the level of confidence (viz. t = 3,36 for six replicates for 99 % confidence).

The limit of quantification (LOQ) or estimated quantitation limit for a given measurement system is typically described as the lowest concentration that can be reliably determined within specified or acceptable limits of precision during routine laboratory operating conditions. The acceptable precision limit is often defined as 10 % relative standard deviation or simply expressed as a fixed multiple (2 to 10) of the method detection limit.

4.6 Test report

The work carried out by the testing laboratory shall be covered by a report that accurately, clearly and unambiguously presents the test results and other relevant information. Each test report shall include at least the following information:

1) Name, address and location of any laboratory involved in the analysis and name of the operator.
2) Date of receipt of sample and date(s) of performance of test(s).
3) Unique identification of report (such as a serial number) and of each page and total number of pages of the report.
4) Description and identification of the sample, including a description of any product disassembly performed to acquire the test sample.
5) A reference to this standard, the method used or performance-based equivalent (including digestion method(s) and equipment).
6) The limit of detection (LOD) or limit of quantification (LOQ).
7) The results of the test expressed as milligrams/kilogram (mg/kg] in samples tested.
8) Any details not specified in this standard which are optional, and any other factors that may have affected the results. Any deviation, by agreement or otherwise, from the test procedure specified here.

The results of all quality control (QC) tests (e.g. results from method blanks, matrix spikes, etc.) and a list of reference materials used and their origin shall be available upon request.

Corrections or additions to a test report after issuance shall be made only in a further document suitably marked, e.g. "Amendment/Addendum to test report serial number XXX" (or as otherwise identified), and shall meet the relevant requirements of 4.2 to 4.6).

4.7 Alternative test methods

Alternative test methods, digestion methods or analytical techniques may be utilized once the performance effectiveness has been validated according to the performance-based measurement system (PBMS) criteria, referenced in the quality control clauses of the test

methods. Any deviation from the described test methods shall be evaluated and documented in the test report.

5 Mechanical sample preparation

5.1 Overview

5.1.1 Field of application

This clause describes common techniques for mechanical size reduction of electrotechnical products, their sub-units or portions thereof, prior to analysis for regulated substances. The test method clauses in this standard have requirements for sample handling and preparation in specific situations. This clause provides general guidance on processing selected portions of an item. The user may elect to apply one or more of the approaches described in this clause to create samples to be submitted for testing. Selection of the appropriate technique(s) depends on the required particle size for the test method to be used. Alternative methods of mechanical sample preparation can be used provided that the required particle size of the sample is achieved without contaminating or compromising the sample with regulated substances.

5.1.2 Quality assurance

Due to the risk of analytical bias resulting from contamination, evaporation of volatile components (e.g. volatilisation due to heat) or from loss of material through dust emissions, it is important to select the appropriate equipment and cleaning procedures.

Contamination can be caused by the grinding equipment and any accessories that contact the sample. For the chosen equipment, it shall be known which elements may be released that will contaminate the analysis sample, e.g. cobalt (Co) and tungsten (W) can be released from tungsten carbide (WC) equipment, and chromium (Cr), nickel (Ni), molybdenum (Mo) and vanadium (V) can be released from stainless steel equipment.

The laboratory shall demonstrate by experiment that a mechanical process does not result in contamination by or loss of detectable amounts of regulated substances. The laboratory shall demonstrate by experiment that the procedure employed for cleaning the mechanical sample preparation equipment prevents contamination of the sample with regulated substances from the previous sample.

This can be demonstrated by processing and analysing certified reference materials and blanks before or after processing a material known to contain significant levels of regulated substances. Certified reference materials are not mandatory. The materials used shall have a known regulated substance content to determine that the mechanical grinding/milling/cutting processes do not cause contamination or loss of regulated substances. The effectiveness of the mechanical sample preparation procedure can be continuously monitored by using quality control practices, including matrix spikes or control samples.

5.2 Apparatus, equipment and materials

The following apparatus, equipment and materials are required:

a) Coarse grinding or cutting mill with 4 mm and 1 mm or similar stainless steel bottom sieve.

b) Centrifugal mill with 25 μm tungsten carbide-coated (WC) steel sieve, and a 6-fold WC-coated rotor (for uniform plastic material a 1 mm steel sieve is appropriate). To avoid the risk of introducing impurities during milling, a 1 mm titanium sieve and a steel/titanium sieve rotor shall be used.

c) “Freezer” bladeless cryogenic impact grinder/mill with self-contained LN_2 tub, insulated case, speed control, programmable timer and safety interlock.

d) Homogenizing mixer (e.g. blender).

e) Analytical balance capable of weighing accurately to 0,000 1 g.

f) Brushes (different sizes).

g) Paper.

h) Scissors, heavy plate shears.

i) Glass beaker.

j) Liquid nitrogen (LN_2).

NOTE Liquid nitrogen is quite volatile and can cause oxygen deficiency in the area of use, especially if the area is enclosed. The laboratory is responsible for ensuring that the proper safety procedures are followed, and that protective equipment is used during cryogenic grinding.

k) Powder funnel.

l) Gloves.

m) Safety glasses.

n) Polyethylene receptacle (for use with LN_2).

5.3 Procedure

5.3.1 Manual cutting

Manual cutting is suitable for rough cutting and preparation of samples for further reduction. Recommended maximum sample sizes are listed below, but will depend on the specification of the equipment used in the subsequent preparation processes.

a) Electronics: Samples are pre-cut to a size of 40 mm × 40 mm using heavy plate shears (5.2 h).

b) Metal sheeting: Samples are pre-cut to a size of 40 mm × 40 mm using heavy plate shears (5.2 h).

c) Polymers: Samples are pre-cut to a size of 5 mm × 5 mm using heavy plate shears or scissors (5.2 h). Thin polymer foil shall be cut into small pieces with shears (5.2 h).

5.3.2 Coarse grinding/milling

Coarse grinding is suitable for reducing samples to approximately 1 mm in diameter. Cool the samples if needed with the LN_2 (5.2.j). For organic samples, cryogenic milling is recommended. An example of cryogenic preparation is to put the samples in a polyethylene receptacle (5.2.n) to cool with LN_2 (5.2.j). Wait until the LN_2 (5.2) has dissipated, plus an additional 10 min thereafter. Grind the samples in the mill (5.2.c) using a 4 mm stainless steel bottom sieve. During grinding, maintain a sample temperature of <–20 °C. Carefully sweep out and collect all particles. Refit the mill (5.2.c) with a pre-weighed 1 mm stainless steel bottom sieve and reprocess the 4 mm material. Carefully sweep out the mill (5.2.c) and collect all particles. Use a 5 min cooling period between grinding cycles.

NOTE It may only be possible to mill metallic materials to a particle size of 4 mm (although 1 mm particles are preferred).

5.3.3 Homogenizing

Homogenizing is suitable for preparing the coarsely ground sample in the mixer prior to further size reduction in the centrifugal mill (5.2.b). Use a container with double the capacity of the amount of powder to be mixed. Set the mixer to its medium speed and mix the powder until it is homogeneous.

5.3.4 Fine grinding/milling

Fine grinding or milling is suitable for reducing samples to <1 mm in diameter. Cool the homogenized sample powder with LN_2 (5.2.j) if needed. For organic samples that have no metal parts, cryogenic milling is recommended. Be careful not to allow the LN_2 (5.2.j) to come into direct contact with the powder in order to prevent spattering and sample loss, e.g. by using a polyethylene receptacle (5.2.n). Mill the sample powder with the centrifugal mill

(5.2.b). Carefully sweep out the centrifugal mill (5.2.n) and collect all the powder. The collected material may be sieved to obtain a sufficiently homogeneous portion of known particle size range.

5.3.5 Very fine grinding of polymers and organic materials

This procedure is suitable for the reduction of samples as small as 500 μm in diameter or less. It is not suitable for metal, glass or similar hard and sharp materials. Approximately 3 g to 10 g of rough-cut (3 mm to 5 mm sections) is placed in the sample vial so that it is about two-thirds to three-quarters full. Add the grinding rod and secure the ends of the vial. Cool the bladeless cryogenic impact grinder (5.2.c) at room temperature for 15 min by filling the reservoir with LN_2 (5.2.j). Place the grinding vials with the samples in the mill (5.2.c) and lock the cover into place. One or more sieves may be added to ensure a sufficiently homogeneous sample.

6 Screening by X-ray fluorescence spectrometry (XRF)

6.1 Overview

This test method describes procedures for the screening analysis of five substances, specifically lead (Pb), mercury (Hg), cadmium (Cd), total chromium (Cr) and bromine (Br) in uniform materials found in electrotechnical products, using the analytical technique of X-ray fluorescence (XRF) spectrometry. It is applicable to polymers, metals and ceramic materials. The test method may be applied to raw materials, individual materials taken from products and “homogenized” mixtures of more than one material. Screening of a sample is performed using any type of XRF spectrometer, providing it has the performance characteristics specified in this test method. Not all types of XRF spectrometers are suitable for all sizes and shapes of sample. Care shall be taken to select the appropriate spectrometer design for the task concerned.

This test method is designed specifically to screen for Pb, Hg, Cd, Cr, Br in uniform materials, which occur in most electrotechnical products. Under typical circumstances, XRF spectrometry provides information on the total quantity of each element present in the sample, but does not identify compounds or valence states of the elements. Therefore, special attention shall be paid when screening for chromium and bromine, where the result will reflect only the total chromium and total bromine present. The presence of Cr(VI) or the brominated flame retardants PBB or PBDE shall be verified by another test method as per Table 1.

When applying this method to electronics “as received”, which, by the nature of their design, are not uniform, care shall be taken in interpreting the results. Similarly, the analysis of Cr in conversion coatings may be difficult due to the presence of Cr in substrate material and/or because of insufficient sensitivity for Cr in typically very thin (several hundred nm) conversion coating layers.

XRF spectrometers can be calibrated to cover a range of mass fractions from the limit of detection in a particular matrix to 100 % composition by mass. XRF spectrometry is a comparative technique; its performance depends on the quality of calibration, which in turn, depends on the quality of the calibrants and the model used to represent the response of the instrument. XRF analysis is subject to matrix effects (absorption and enhancement) as well as spectral interferences.

The performance of this test method has been tested for the following substances in various media and within the concentration ranges as specified in Tables 2 to 6.

Table 2 – Tested concentration ranges for lead in materials

Substance/element	Lead						
Parameter	Unit of measure	Medium/material tested					
		ABS	PE	Low-alloy steel	Al-Si alloy	Tin-based alloy	Glass	Ground PWB
Concentration or concentration range tested	mg/kg	109 to 184	14 to 108	30	190 to 930	174	240 000	22 000 to 23 000

Table 3 – Tested concentration ranges for mercury in materials

Substance/element	Mercury		
Parameter	Unit of measure	Medium/material tested	
		ABS	PE
Concentration or concentration range tested	mg/kg	100 to 940	4 to 25

Table 4 – Tested concentration ranges for cadmium in materials

Substance/element	Cadmium			
Parameter	Unit of measure	Medium/material tested		
		Tin-based alloy	ABS	PE
Concentration or concentration range tested	mg/kg	3	11 to 107	22 to 141

Table 5 – Tested concentration ranges for total chromium in materials

Substance/element	Chromium					
Parameter	Unit of measure	Medium/material tested				
		ABS	PE	Low-alloy steel	Al-Si alloy	Glass
Concentration or concentration range tested	mg/kg	28 to 270	18 to 115	240	130 to 1 100	94

Table 6 – Tested concentration ranges for bromine in materials

Substance/element	Bromine			
Parameter	Unit of measure	Medium/material tested		
		PS-HI, ABS	PC/ABS	PE
Concentration or concentration range tested	mg/kg	99 138 to 118 400	800 to 2 400	98 to 808

These substances in similar media outside of the specified concentration ranges may be analysed according to this test method; however, the performance has not been established for this standard.

There are two principal calibration methods in XRF spectrometry:

- A universal calibration can be performed using fundamental parameters (FP) approaches. FP approaches can be calibrated with pure elements or compounds or with a small

number of reference materials with well defined matrix compositions. As with all XRF calibrations, accuracy can be expected to improve when the calibrants are increasingly similar to the samples.

- An empirical calibration can be created using reference materials in combination with a calibration algorithm capable of correcting for the matrix and spectral interferences. In principle, an empirical calibration is valid only for the specific material matrix for which it was created, with multiple calibrations needed for analyses of multiple matrices. However, for the purposes of the screening test, it may be possible to apply the same empirical calibration for materials of similar matrices. The calibrants shall cover the entire range of each element in the matrix. If a potential interfering element is not included in the calibration model, its presence in a sample may cause a significant bias. Due to the limited availability of calibrants, i.e. reference materials, it is a complex or often impossible task to include all possible matrix and spectral interferences in a method while maintaining optimum accuracy.

For coated materials and multilayered structures, accurate results cannot be obtained without prior knowledge of the layered structure and the use of a calibration model that accounts for the structure of the sample. In the case of a coating or thin layer, special care shall be taken to ensure that the XRF spectrometer has sufficient sensitivity to detect the small quantity of substance in the layer. Shall the sensitivity of the XRF spectrometer be insufficient to measure the regulated substance directly in the coating, one may resort to physical removal of coating layer from the substrate to accumulate enough material for analysis.

Screening analysis can be carried out by one of two means:

- Non-destructively – by directly analysing the sample “as received”.
- Destructively – by applying one or more mechanical or chemical sample preparation steps prior to analysis.

In the latter case the user shall apply the procedure for sample preparation as described in Clause 5. This test method will guide the user in choosing the proper approach to sample presentation.

6.1.1 Principle

To achieve its purpose, this test method shall provide rapid, unambiguous identification of the elements of interest. The test method shall provide at least a level of accuracy that is sometimes described as semi-quantitative, i.e. the relative uncertainty of a result is typically 30 % or better at a defined level of confidence of 68 %. Some users may tolerate higher relative uncertainty, depending on their needs. This level of performance allows the user to sort materials for additional testing. The overall goal is to obtain information for risk management purposes.

This test method is designed to allow XRF spectrometers of all designs, complexity and capability to contribute screening analyses. However, the capabilities of different XRF spectrometers cover such a wide range that some will be relatively inadequate in their selectivity and sensitivity while others will be more than adequate. Some spectrometers will allow easy measurement of a wide range of sample shapes and sizes, while others, especially research-grade WDXRF units, will be very inflexible in terms of test portions.

Given the above level of required performance and the wide variety of XRF spectrometers capable of contributing useful measurements, the requirements for the specification of procedures are considerably lower than for a high-performance test method for quantitative determinations with low estimates of uncertainty.

This test method is based on the concept of performance-based methods. Apparatus, sample preparation and calibration are specified in this standard in relatively general terms. It is the responsibility of the user to document all procedures developed in the laboratory that uses the test method. The user shall establish a written procedure for all cases denoted in this method by the term “work instructions”.

This method carefully stipulates spectrometer and method performance parameters that shall be documented by the user.

6.1.2 Warnings

WARNING 1 Persons using the XRF test method shall be trained in the use of XRF spectrometers and have a working knowledge of the technique and sampling requirements.

WARNING 2 X-rays are hazardous to humans. Care shall be taken to operate the equipment in accordance with both the safety instructions provided by the manufacturer and the applicable local health and occupational safety regulations.

6.2 Apparatus, equipment and materials

6.2.1 XRF spectrometer

An XRF spectrometer consists of an X-ray excitation source, a means of reproducible sample presentation, an X-ray detector, a data processor and a control system.

a) Source of X-ray excitation – X-ray tube or radioisotope sources are commonly used.
b) X-ray detector (detection subsystem) – Device used to convert the energy of an X-ray photon to a corresponding electric pulse of amplitude proportional to the photon energy.

6.2.2 Materials and tools

Materials used in the preparation of samples for XRF measurements shall be shown to be free of contamination, specifically by the analytes of this test method. This means that all grinding materials, solvents, fluxes, etc. shall not contain detectable quantities of Pb, Hg, Cd, Cr and/or Br.

Tools used in the handling of samples shall be chosen to minimize contamination by the analytes of this test method as well as by any other elements. Any procedures used to clean the tools shall not introduce contaminants.

6.3 Reagents

Reagents shall not contain detectable quantities of Pb, Hg, Cd, Cr and/or Br.

6.4 Sampling

It is the responsibility of the user of this test method to define the test sample using documented work instructions. The user may choose to define the test sample in a number of ways, either via a non-destructive approach in which the portion to be measured is defined by the viewing area of the spectrometer, or by a destructive approach in which the portion to be measured is removed from the larger body of material and either measured as is or destroyed and prepared using a defined procedure.

6.4.1 Non-destructive approach

The user of this test method shall:

a) Establish the area viewed by the spectrometer and place the test sample within that area, taking care to ascertain that no fluorescent X-rays will be detected from materials other than the defined test portion. Usually, the area viewed by spectrometer is delineated by the shape and boundary of the measuring window of the instrument.
b) Make every effort to establish repeatable measurement geometry with a repeatable distance between the spectrometer and the test portion.

c) Take all practical steps to identify a test portion with as regular shape as possible, taking into consideration flatness across the entire area, surface roughness and known physical structure.

d) Document steps taken to disassemble a larger object to obtain a test portion.

6.4.2 Destructive approach

The following points shall be taken into account in the destructive approach:

a) The user shall create and follow a documented work instruction for the means of destruction applied to obtain the test portion as this information is critical for correct interpretation of the measurement results.

b) A procedure that results in a powder shall produce a material with a known or controlled particle size. In cases where the particles have different chemical, phase or mineralogical compositions, it is critical to reduce their sizes sufficiently to minimize differential absorption effects.

c) In a procedure that results in a material being dissolved in a liquid matrix, the quantity and physical characteristics of the material to be dissolved shall be controlled and documented. The resulting solution shall be completely homogeneous. Instructions shall be provided to deal with undissolved portions to ensure proper interpretation of the measured results. Instructions shall be provided for presentation of the test portion of the solution to the X-ray spectrometer in a repeatable manner, i.e. in a liquid cell of specified construction and dimensions.

d) In a procedure that results in a sample material being fused or pressed in a solid matrix, the quantity and physical characteristics of the sample material shall be controlled and documented. The resulting solid (fused or pressed pellet) shall be completely uniform. Instructions shall be provided to deal with unmixed portions to ensure proper interpretation of the measured results.

6.5 Procedure

6.5.1 General

The test procedure covers preparation of the X-ray spectrometer, preparation and mounting of test portions and calibration. Certain instructions are presented in general terms due to the wide range of XRF equipment and the even greater variety of laboratory and test samples to which this test method will be applied. However, a cardinal rule that applies without exception to all spectrometers and analytical methods must be followed; that is that the calibration and sample measurements must be performed under the same conditions and using the same sample preparation procedures.

In view of the wide range of XRF spectrometer designs and the concomitant range of detection capabilities, it is important to understand the limitation of the chosen instrument. Certain designs may be incapable of detecting or accurately determining the composition of a very small area or very thin samples. As a consequence, it is imperative that users carefully establish and clearly document the performance of the test method as implemented in their laboratories. One goal is to prevent false negative test results.

6.5.2 Preparation of the spectrometer

Prepare the spectrometer as follows:

a) Switch on the instrument and prepare it for operation according to the manufacturer's manual. Allow the instrument to stabilize as per guidelines established by the manufacturer or laboratory work instructions.

b) Set the measurement conditions to the optimum conditions previously established by the manufacturer or the laboratory.

NOTE Many instruments available on the market are already optimized and preset for a particular application, and therefore this step might not be necessary. Otherwise, the laboratory should establish optimum operating conditions for each calibration. Choices should be made to optimize sensitivity and minimize spectral interferences.

Excitation conditions may vary by material, analyte and X-ray line energy. A list of recommended analytical X-ray lines is given in Table 7. Detection system settings should optimize the compromise between sensitivity and resolution. Guidance can usually be found in the instrument manual and in literature on X-ray spectrometry.

Table 7 – Recommended X-ray lines for individual analytes

Analyte	Preferred line	Secondary line
Lead (Pb)	L_2–M_4 ($L\beta_1$)	L_3–$M_{4,5}$ ($L\alpha_{1,2}$)
Mercury (Hg)	L_3–$M_{4,5}$ ($L\alpha_{1,2}$)	
Cadmium (Cd)	K–$L_{2,3}$ ($K\alpha_{1,2}$)	
Chromium (Cr)	K–$L_{2,3}$ ($K\alpha_{1,2}$)	
Bromine (Br)	K–$L_{2,3}$ ($K\alpha_{1,2}$)	K–$M_{2,3}$ ($K\beta_{1,3}$)

NOTE 1 Other X-ray line choices may provide adequate performance. However, when deciding on alternative analytical lines one should be aware of possible spectral interferences from other elements present in the sample (e.g. BrKα on PbLα or AsKα on PbLα lines; see D.1b) for more typical examples).

NOTE 2 K–$L_{2,3}$ ($K\alpha_{1,2}$) means that there are actually two transitions to the K shell, i.e. one from the L_2 shell which generates $K\alpha_2$ X-rays and another from the L_3 shell that generates K α_1 X- rays. However, since both energies are very close, energy dispersive spectrometers cannot distinguish them and so they are analysed as one combined K $\alpha_{1,2}$ energy.

6.5.3 Test portion

The creation of a test portion is described in 6.4.

In the case of destructive sample preparation, measure the mass and dimensions of the test portion as required by the calibration method and the work instruction established by the laboratory to ensure repeatable sampling.

6.5.4 Verification of spectrometer performance

Spectrometer performance shall be verified as follows:

a) Users shall provide objective evidence of the performance of the method as implemented in their laboratories. This is necessary to enable the users and their customers to understand the limitations of the method and to make decisions using the results of analyses. Critical aspects regarding the performance of the method are as follows:
   - spectrometer performance:
     - sensitivity for each analyte,
     - spectral resolution,
     - limit of detection,
     - demonstration of measured area,
     - repeatability of sample preparation and measurement,
     - accuracy of calibration, which will be checked according to 6.8.

   Given the variety of spectrometers and the associated software operating systems, it is acceptable for the users to obtain this information in their own laboratory using their own procedures or as a service provided by the manufacturer. It is important to obtain verification of spectrometer and method performance when the method is implemented. Evidence of the maintenance of performance may be obtained through the use of control charts or by repeating the measurements and calculations made on implementation.

b) Spectrometer sensitivity is used as a figure of merit to compare spectrometers and to ensure that a meaningful calibration is possible.

c) Spectral resolution is important to ensure that the analyte and interfering spectral lines are handled correctly in the collection of data and in the calibration. For the purposes of this standard, the correction of line overlaps is considered as part of the spectrometer calibration.

d) The limit of detection, LOD, shall be estimated for each set of operating conditions employed in the test method using Equation (1) below:

$$LOD = 3\sigma \quad (1)$$

where

LOD is the limit of detection (LOD) expressed in units of concentration;

σ is the standard deviation of the results of multiple determinations using a blank material. Standard deviation is usually estimated using a small (but not less than seven) number of determinations, in which case the symbol, *s* (the unbiased estimate of standard deviation, σ) is substituted for σ.

NOTE The limit of detection is a critical parameter that tells the user whether the spectrometer is being operated under conditions that allow the detection of an analyte at levels sufficiently below the allowed substance limits to be useful for making decisions. Limit of detection is a function of the measurement process of which the material is a significant part. If the measurement process changes when the material is changed, the limits of detection may also change. For optimum performance, the limit of detection should be equal to or less than 30 % of the laboratory's own action limits established to provide maximum acceptable risk of non-compliance.

e) Demonstration of the measured area is important to ensure that the viewed area is known for the spectrometer equipped with any accessories that define X-ray beam size, shape and location. In many cases, the beam size, shape and location define the test portion. The laboratory or the manufacturer shall provide a means to define the beam size and shape and identify its location on the test portion.

f) Repeatability of sample preparation and measurement is an important parameter to demonstrate that the test method has statistical control. If destructive sample preparation precedes the measurement, the repeatability shall be tested, including sample preparation, otherwise repeatability of the measurement shall be tested on the same sample. Repeatability is expressed as the standard deviation of at least seven measurements of a prepared sample using the optimum spectrometer operating conditions. Repeatability shall be measured for each analyte in a test portion containing a concentration of the analyte greater than five times the limit of detection estimated in 6.5.4.

6.5.5 Tests

Place the test portion in the correct position for measurement with the XRF spectrometer. If necessary, establish the required atmosphere in the chamber of the spectrometer and allow it to stabilize.

NOTE The measurements are typically made in an air atmosphere. However, should there be a need to measure light elements such as S, Al, etc., it may be advantageous to measure in a vacuum or helium (A.3.b) atmosphere.

Measure the test portion by collecting sufficient numbers of X-ray counts to attain a counting statistical uncertainty less than the established relative standard deviation for measurement repeatability (see 6.5.4). The settings of the XRF spectrometer for analysis of the test portion shall be identical to those used for calibration measurements.

6.5.6 Calibration

The analytical method shall be calibrated taking into account matrix effects and other effects that influence the determination of the intensity of the fluorescence radiation. A list of these effects is given in Annex D.

There are two principal calibration options in XRF spectrometry:

- Fundamental parameters approaches employing a range of calibrants:
  - pure elements and pure compounds, or
  - synthetic mixtures prepared from pure substances, or
  - individual reference materials representing each material to be analysed.
- Empirical (traditional) calibration using a model based on influence coefficients obtained

– using empirical data from a suite of calibrants similar to the unknowns, or

– using a fundamental parameters approach.

Follow the guidelines in the manufacturer's manual when selecting the calibration options available in the operating system software.

Depending on the instrument, the user may or may not be required to perform the calibration. There are commercially available instruments which are already optimized, calibrated and preset for specific applications. These instruments do not require calibration by the analyst.

The choice of calibrants depends in part on the choice of calibration model. For empirical options, the calibrants shall be similar in matrix composition to the materials to be analysed. In the set of calibrants, element concentrations shall cover the range of concentration expected in the samples and they shall vary independently of one another. If the calibration covers many elements in a wide range of concentrations, a large number of calibration samples may be necessary. The minimum number of calibrants for an empirical method is $2(n+2)$, where n = the number of analytes.

A fundamental parameters calibration approach can significantly reduce the number of calibration samples. Fundamental parameters software allows the user to calibrate the sensitivity of each element using pure elements and compounds. As an alternative to pure calibrants, the software will typically allow the use of a small number of reference materials more similar to the samples. Enhancements of the method include the use of scattered radiation to correct for certain matrix or sample morphology effects.

6.6 Calculations

The following calculations shall be performed as necessary when using this test method:

a) In contemporary instruments the calculations are typically performed automatically by the spectrometer operating system software. If calculations are to be done by hand, the algorithms and all the parameters shall be specified in the work instructions for the test method. Calculate the result for each analyte, in per cent by mass, in each test portion using the calibration model established for the sample type.

b) If the test portion has been prepared by dilution, calculate the result on the basis of the original test sample using the appropriate dilution factor.

Estimate the uncertainty of the results using one of the following methods and compare the result to the maximum allowed concentration of the analyte in the material.

c) The preferred method is to create an uncertainty budget for each calibration implemented in the test method. The uncertainty budget shall be compliant with ISO/IEC Guide 98. Express the expanded uncertainty estimate at the 95 % confidence level.

NOTE 1 It is an oversimplification to assign the uncertainty as some multiple of the repeatability standard deviation of replicate determinations. Under certain circumstances, XRF measurements can be exceedingly precise, leading to an estimated uncertainty that is too small to cover all sources of error. This approach ignores important contributions from the calibrants, the mathematical model used to fit the calibration curve and the potential for the introduction of bias during sample preparation. Moreover, the definition of an uncertainty budget is beyond the scope of this standard.

d) This method recognizes that it may be impractical or impossible to perform a proper uncertainty budget. Therefore, as an alternative, choose a safety factor greater than or equal to the expected expanded uncertainty for each analyte at the level of the maximum allowed concentration. It has been agreed, for the purpose of this test method, that it is suitable to assume a relative uncertainty of 30 % in a result obtained for a sample containing the maximum allowed value for the element in the material in question. In practice, this assumption can be used to define a confidence interval around the maximum allowed concentration value, which can be used for the purpose of making decisions regarding the need for additional testing.

NOTE 2 The use of a safety factor is an over-simplification due in part to the fact that, in most cases, relative uncertainty is a function of concentration. Typically, relative uncertainty increases rapidly as the analyte concentration decreases. The analyst is cautioned not to interpret the 30 % safety factor as a relative uncertainty

of results of determinations. The analyst is also cautioned to re-evaluate the safety factor if the detection limit is greater than 20 % relative to the maximum allowed concentration, or if the maximum allowed concentration is reduced by the regulating authority.

6.7 Evaluation of the method

The detailed summary results for each substance and material tested using XRF are listed in Tables D.3 to D.7 (see Annex D). Only these results shall be a basis for any conclusions about the method performance.

The following general conclusions can be made, based on the results summarized in the tables and the analysis of data from the IIS2. The summary conclusions of this method performance for each tested substance and material are given in the following subclauses:

a) Evaluation of the results and method performance can only be fragmentary because of the shortage of CRMs to fully cover the required ranges of concentrations and types of materials.

b) Due to the limited amounts of available CRMs, not all laboratories tested all samples; consequently, the results are not always directly comparable.

c) The samples were analysed “as received”, that is no sample preparation was involved.

d) Precisions reported by individual laboratories for individual results were typically at much less than 5 % relative standard deviation (RSD).

e) The participating laboratories used various calibration methods, such as empirical, Compton normalization and methods based on fundamental parameters.

f) It is imperative that the method performance be further researched and tested during interlaboratory studies.

6.7.1 Lead

The average inaccuracy of Pb determination in polymers above a level of 100 mg/kg was better than ± 13 % relative and the imprecision was better than ± 19 % relative. At a Pb concentration of 10 mg/kg, the inaccuracy and imprecision were ± 30 % relative and ± 70 % relative, respectively. In Al alloys, the inaccuracy and imprecision were less than ± 10 % relative and ± 25 % relative, respectively. A Pb concentration of 174 mg/kg in tin-based alloy produced inconclusive results ranging from 60 mg/kg to 380 mg/kg. 30 mg/kg of Pb in an alloy steel was not detected.

The results for ground PWBs point to possible non-homogeneity of the material as the source of great imprecision and inaccuracy of the results.

6.7.2 Mercury

The average inaccuracy of Hg determination in polymers at or below 1 000 mg/kg was better than ± 10 % relative, while the imprecision was better than ± 25 % relative. No alloy material was tested for Hg.

6.7.3 Cadmium

The average inaccuracy of Cd determination in polymers at or above 100 mg/kg was ± 10 % relative, and the imprecision was better than ± 15 % relative. At a level of 20 mg/kg Cd, the inaccuracy varied from ± 10 % to ± 50 % relative, and the imprecision varied from 20 % to 100 % relative. A level of 3,3 mg/kg of Cd in tin-based alloy was not detected by any instrument.

6.7.4 Chromium

The average inaccuracy of total Cr determination in polymers at or below 115 mg/kg was observed to be better than 17 % relative while the imprecision was about ± 30 % relative. For a similar concentration level in glass, the inaccuracy and imprecision for total Cr were better

than ± 20 % relative and 35 % relative respectively. In aluminium alloys at 1 100 mg/kg Cr, the inaccuracy and imprecision were ± 10 % relative and better than ± 41 % relative, respectively. A Cr concentration of about 100 mg/kg in Al alloy was not detected.

6.7.5 Bromine

Based on the CRMs, the average inaccuracy of determination of total Br concentration in polymers at or below 1 000 mg/kg was better than ± 10 % relative, and the standard deviation was better than ± 13 % relative. At elevated Br concentrations of 10 %, inaccuracy was better than ± 25 % relative and imprecision was about ± 30 % relative. These latter results reflect the inadequacy of empirical calibrations for high Br concentrations.

Generally, the inaccuracy and imprecision of analysis for all of the five elements were better than ± 20 % relative for concentrations above 100 mg/kg in polymers and aluminium alloys.

6.8 Quality control

6.8.1 Accuracy of calibration

The following steps shall be taken to validate the accuracy of calibration:

a) The accuracy of each calibration shall be validated by analysing one or more reference materials representative of each material used in the implementation of this test method. Analyte concentration levels in the reference materials shall be within one order of magnitude of the maximum allowed values for the analyte in the material. Ideally, reference materials will be available to bracket the maximum allowed values.

b) Results of measurements of the reference materials shall be calculated and expressed according to 6.6, including an estimate of uncertainty.

c) Apply a bias test to the results and the certified or reference values assigned to the reference materials. The bias test shall take into account the uncertainty of an assigned value.

NOTE For guidance on bias tests, refer to the National Institute of Standards and Technology Special Publication 829[6] or similar documents.

d) If a bias is detected, correct the calibration and repeat the determinations.

6.8.2 Control samples

Control samples shall be prepared and used as follows:

a) Designate a quantity of stable material as the control sample for each calibration. Preferably, this shall be a solid in the form of a disc (pellet).

b) Prepare a test portion of the control sample and subject it to testing using each of the calibrations as soon as they have been validated. Do this at least four times. Calculate the average and standard deviation and use these values to establish a control chart for each analyte in each calibration. Control samples may be created by the analysts. Some instrument manufacturers provide control sample(s) with their equipment.

c) At appropriate time intervals, prepare a test portion of the control sample and subject it to testing using each of the calibrations implemented in the test method. Compare the results to the control chart limits. If the results violate accepted rules for control, troubleshoot the test methods, correct the problem and perform a test on a new control sample.

6.9 Special cases

6.9.1 Presentation of a sample for measurement

The procedure for presentation of a sample for measurement is as follows:

a) If the measurement is to be performed on an instrument with an analysis chamber, a section including the sample to be measured shall be placed inside the sample chamber of the X-ray fluorescence spectrometer. The total sample shall be mounted in such a way that the target sample can be properly located in the measuring position. If the sample does not fit properly in the chamber, it shall be cut to the appropriate size for measurement.

b) If the measurement is performed with a portable hand-held XRF analyser, care shall be taken to ensure that the measuring aperture covers the section to be examined.

c) Analysis of samples which are not flat or large enough to cover the measuring aperture of the spectrometer (such as small screws) may be handled by certain fundamental parameters methods which are designed to compensate the results for oddly shaped samples. In such a case, and following the manufacturer's recommendations, the analyst shall carefully position one or more of the items in the proper holder prior to measurement and shall obtain an estimate of the composition using the software tools provided by the method.

d) The analysis of thin samples is complicated by the dependence of measured count rates on the analyte concentration in the sample and on sample thickness. The analyst shall be aware of the structure and composition of the item within the measured area.

6.9.2 Uniformity of the sample

Uniformity, from the point of view of XRF analysis, depends on the physical uniformity of the composition of the tested material within the volume of material irradiated by the instrument during the test. One or more of the following three categories may apply when determining the uniformity of the sample:

a) Large surface area samples (applies to all samples):

   The assessment of uniformity of the tested material for the purposes of XRF analysis is made by visual inspection and with the aid of any additional information. For example, any object that appears uniform in colour, shape and appearance is most likely uniform, and would not require mechanical destruction before analysis. Typical examples may be large, extended plastic objects such as plastic enclosures, thick tape, metal alloys, etc. Any additional information about the tested object shall be used to establish its uniformity. For example, many plastic enclosures, and even more so metal enclosures, are painted. Plastic enclosures may be metallized, often on the inside. In such cases the test shall be performed on an unpainted or a non-metallized fragment, which may require some degree of disassembly, although not the destruction, of the object. Metal parts may be plated with another metal, such as zinc on steel, Cd on steel, or Cr on steel and Al. These will be indicated by relatively very high readings of plating metals, with the possible exception of Cr, as Cr coatings are typically very thin. All coatings shall be removed when attempting to analyse the base material.

b) Small area samples:

   Small individual electronic parts or segments may be analysed in situ without the need for separation, as long as an instrument is used that has sufficient lateral and depth resolution to probe only the intended material without spill-over into adjacent areas. The sample shall appear uniform, such as plastic encapsulation, individual soldering lead or isolated areas of polymer/epoxy. Special care shall be taken to avoid the complications of interference by metal plating, polymer coating or paint when analysing the base material. Any coatings shall be physically removed.

c) Coatings and thin samples:

   Samples that are too small or very thin may easily violate the condition of minimum sample thickness or mass required for the results to be valid. In such instances, a number of small objects of the same kind (for example small screws) shall be placed in a sample cup and only then analysed. Similarly, thin samples of the same kind shall be stacked in a pile thick enough to fulfil the minimum sample thickness criterion and analysed accordingly. As a general rule, all samples shall completely cover the measuring window/area of the spectrometer. The sample shall have a minimum thickness of 5 mm in the case of polymers and light alloys such as Al, Mg or Ti, 15 mm in the case of liquids and about 1 mm for all other alloys.

These rules may not apply if the analytical software of the instrument allows effective correction of results for variable thickness, shape and size of analysed samples.

The insulation on thin wires and ribbon cables may not be treated as uniform and shall be measured by extracting the metal conductor first. On the other hand, almost all power cords of a diameter larger than 5 mm with copper wiring inside may be treated as uniform for the purpose of insulation analysis. The metal may also be analysed after separation. Some metal coatings may be analysed if the user knows the construction of the material, and the spectrometer is calibrated to analyse such a complex layer system. For example, the coating is known to be SnAgCu (tin-silver-copper alloy) (plated over) copper (plated over) epoxy. The tin alloy may be analysed, provided the instrument is calibrated for this specific sample type. It is commonly accepted that most XRF instruments will not detect, with sufficient sensitivity, Cr in conversion coatings unless they are at least a few hundred nanometres in thickness. Due to variations of the required sample size from instrument to instrument, the operator of the spectrometer is advised always to consult the instrument manual or manufacturer to know the requirements of minimum size/mass/thickness conditions of the sample.

d) The numerical screening limits listed (see Table D.2) may not be appropriate to determine regulatory compliance of all possible samples, particularly if the sample is a composite of different product materials. This may especially be the case for samples that have been blended into a “homogenized” state, or for small amounts of homogeneous material such as thin coatings. This method refers to uniformity for the sake of accurate XRF analysis and does not attempt to make a “legal” determination of sampling requirements.

e) Summary:

The tested object may be considered as uniform and analysed non-destructively if

– it is not painted or plated and appears to the naked eye to be the same colour and consistency throughout,

– it is not otherwise known to be non-uniform in its construction or design,

– the top layer of a thin coating can be analysed separately from the base material in a known matrix only, and the instrument is calibrated for this known matrix.

f) When using any XRF instrument, it is recommended that the object be tested in more than one area if the design allows. Any statistically significant differences between the measurements may indicate possible non-uniformity. If in doubt as to the uniformity of the tested material, a destructive analysis is recommended.

7 Determination of mercury in polymers, metals and electronics by CV-AAS, CV-AFS, ICP-OES and ICP-MS

7.1 Overview

This clause describes the test method for the determination of mercury (Hg) in materials used in electrotechnical products. These materials are polymers, metals and electronics (e.g. printed wiring boards, cold cathode fluorescent lamps, Hg switches). Batteries containing Hg shall be handled as described in [22]. The interlaboratory study has only evaluated these test methods for plastics, other matrices have not been covered.

The clause describes the use of four methods, namely CV-AAS (cold vapour atomic absorption spectrometry), CV-AFS (cold vapour atomic fluorescence spectrometry) ICP-OES (inductively coupled plasma optical emission spectrometry), and ICP-MS (inductively coupled plasma mass spectrometry) and several procedures for preparing the sample solution from which the most appropriate method of analysis can be selected by experts. CV-AAS is the preferred method due to its sensitivity and ease of use.

Analysis by CV-AAS, CV-AFS, ICP-OES and ICP-MS allows the determination of the target element, Hg, with high precision (uncertainty in the low per cent range) and/or high sensitivity (down to the µg/kg level). The test procedures described in this clause are intended to provide the highest level of accuracy and precision for concentrations of mercury in the range from 4 mg/kg to 1 000 mg/kg. The procedures are not limited for higher concentrations.

An appropriate mass of cryogenically milled and homogenized sample is digested in a concentrated acid solution under fixed temperature or pressure conditions. After digestion, the sample solution shall be stored at 4 °C to minimize evaporation. For longer-term storage of Hg, it is recommended that the solutions be spiked with 1 to 2 drops of potassium permanganate solution.

Finally, in the digestion solution obtained, Hg is determined by CV-AAS, CV-AFS, ICP-OES or ICP-MS. For ICP-OES, and IPC-MS, the digestion solution may be analysed without any further preparation. When using CV-AAS and CV-AFS, the Hg is reduced to the elemental state before it is analysed.

The samples for analysis have to be mechanically pre-prepared before chemical digestion. In order to fulfil the minimum requirements for an accurate analysis, the maximum particle size and minimum amounts of sample shall be given in the test report. It is highly likely that after digestion, solid residues will be present. It shall be ensured that no target elements are included in these residues. This standard strongly recommends the use of a heating digester, equipped not only with vessels and reflux coolers, but also with absorption vessels or a microwave digestion system. This sophisticated equipment avoids losses of high-volatile Hg. Nevertheless, if the user can ensure the suitability of a simpler approach, it may be applied. Any deviation from the described procedures shall be evaluated and documented in the test report.

This procedure is recommended for use by laboratory assistants and/or technicians working under the close supervision of chemists experienced in the sample preparation requirements for inorganic analyses, and by chemists working independently.

The following points shall be taken into account:

- Many Hg compounds are highly toxic if swallowed, inhaled or absorbed through the skin. Extreme care shall be exercised in the handling of concentrated Hg reagents. Because of the risk of Hg in some laboratory environments, all lab ware and sample collection tools shall be stored in a clean, Hg-free environment.
- All operations prior to instrument analysis shall be carried out in the fume hood.
- A condenser shall be used to prevent volatilization under the test conditions.
- The microwave oven shall be operated strictly according to the supplier’s instructions.

7.2 Apparatus, equipment and materials

In general, the collection and storage of glassware are a critical part of Hg analysis, regardless of the type of sample to be analysed. Because of the sensitivity of the Hg analysis techniques described, each individual sampling step shall be carried out with great care. All sampling, storage and manipulation apparatus shall be Hg-free. Soak all glassware in 50 % (m/m) nitric acid (7.3.c) for 24 h at room temperature, and then rinse thoroughly with water (7.3.a).

The following equipment shall be used:

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

For wet digestion as described in 7.4.2:

b) Heating digester equipped with reaction vessels, reflux coolers and absorption vessels (for the digestion of metals and electronics);

c) Glass fibre filter 0,45 μm.

For microwave digestion as described in 7.4.3:

d) Microwave sample preparation system equipped with a sample holder and high-pressure polytetrafluoroethylene/tetrafluoroethylene modified (PTFE/TFM) or perfluoro alkoxyl

alkane resin/tetrafluoroethylene modified (PFA/TFM) or other vessels based on fluorocarbon materials (for the digestion of metals containing significant amounts of silicon (Si), zirconium (Zr), hafnium (Hf), titanium (Ti), tantalum (Ta), niobium (Nb) or tungsten (W), and for plastics);

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

f) Volumetric flasks such as 25 ml, 250 ml, etc. (PTFE-PFA equipment or glassware). Where appropriate, other types of volumetric equipment with acceptable precision and accuracy can be used as alternatives to volumetric flasks.

g) Pipettes such as 1 ml, 2 ml, 5 ml, 10 ml, etc. (PTFE-PFA equipment or glassware).

h) Micropipettes such as 200 µl, 500 µl, 1 000 µl, etc.

i) Plastic containers for standards and digestion solutions.

j) Cold vapour atomic absorption spectrometer (CV-AAS).

k) Cold vapour atomic fluorescence spectrometer (CV-AFS).

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

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

n) Argon gas with a purity of at least 99,99 % (v/v).

7.3 Reagents

For the determination of elements at trace level, the reagents shall be of adequate purity. Contamination can be a major source of error when working in the 1 ng range with the instruments. Cautious handling of the apparatus and careful technique will minimize this problem. Therefore, only grade 1 water (7.3.a) shall be used. Care shall be taken that all materials in contact with the water are Hg-free.

Chemicals used for sample preparation can be a major source of contamination. Only reagents that are Hg-free shall be used. It is therefore highly recommended that the blank values of the reducing agents and the other chemicals be measured before using them for sample preparation. Beakers, pipettes volumetric flasks, etc. are all major sources of metal contamination. It is essential to use Hg-free plastic or quartz glassware for sample handling.

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

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

b) Nitric acid (concentrated nitric acid): $\rho(HNO_3)$ = 1,4 g/ml, 65 % (m/m), “trace metal” grade.

c) Nitric acid, 50 % (m/m), “trace metal” grade.

d) Nitric acid, 0,5 mol/l, “trace metal” grade.

e) Nitric acid, 1 % (m/m), “trace metal” grade.

f) Nitric acid, 1,5 % (m/m), “trace metal” grade.

g) Nitric acid, 5 % (m/m) “trace metal” grade.

h) Fluoroboric acid: HBF_4, 50 % (m/m), “trace metal” grade (for microwave digestion).

i) Hydrogen peroxide: H_2O_2, 30 % (m/m), “trace metal” grade (for microwave digestion).

j) Standard solution with 1 000 mg/ml of Hg, “trace metal” grade.

k) Potassium tetrahydridoborate (potassium borohyride): KBH_4, “trace metal” grade.

l) Potassium permanganate: $KMnO_4$, 5 % solution (m/v), “trace metal” grade. Dissolve 5 g of potassium permanganate in 100 ml of water (7.3.a).

m) Sodium tetrahydridoborate (sodium borohydride), $NaBH_4$, “trace metal” grade.

n) Sodium hydroxide, NaOH (“trace metal” grade).

o) Internal standard solution, “trace metal” grade:

- 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.
- For use with ICP-OES, Sc or Y are recommended. The recommended concentration is 1 000 mg/l.
- For use with ICP-MS, Rh is recommended. The recommended concentration is 1 000 µg/l.

p) Reducing agent for CV-AAS: 3 % (m/v) $NaBH_4$ in 1 % (m/v) NaOH.

Add approximately 800 ml of water (7.3.a) to a 1 l volumetric flask, followed by the addition of 10,0 g sodium hydroxide (7.3.n). Add 30,0 g of sodium tetrahydridoborate powder (7.3.m), stir until dissolved, fill up to the mark with water (7.3.a) and filter. Prepare daily.

NOTE 1 A reductant solution containing sodium tetrahydridoborate in a sodium hydroxide solution is recommended. If the available Hg hydride system cannot deal with this reductant, tin (II) chloride can be used instead. The instructions given in the operator's manual for the instrument should be followed.

q) Reducing agent for CV-AFS: 1 % (m/v) KBH_4 in 0,05 % (m/v) NaOH.

Add approximately 800 ml of water (7.3.a) to a 1 l volumetric flask followed by the addition of 0,50 g sodium hydroxide (7.3.n). Add 10,0 g of potassium tetrahydridoborate 7.3.k), stir until dissolved, fill up to the mark with water (7.3.a) and filter. Prepare daily.

NOTE 2 A reductant solution containing potassium tetrahydridoborate in a sodium hydroxide solution is recommended. If the available Hg hydride system cannot deal with this reductant, tin (II) chloride can be used instead. The instructions given in the operator's manual for the instrument should be followed

7.4 Sample preparation

7.4.1 Test portion

The different test methods, which can be used as alternatives according to this standard, need different amounts of sample to obtain the required quality of results.

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 Clause 5).

Cold cathode fluorescent lamps (CCFL) and samples containing liquid Hg shall be frozen and then crushed before they can be handled as described in this clause. It is recommended that the instructions of California EPA SOP No. 914-S[21] be followed.

For the determination of Hg in single-ended fluorescent lamps (compact fluorescent lamps), follow the instructions given in Annex E of 2002/747/EC[20].

For (longer) double-ended fluorescent lamps, freezing of the complete lamp is almost impossible. In this case, a procedure is given in JEL303-2004, 4.1.3.1 ff[19].

The resulting concentrated solutions may be measured directly by ICP-OES and ICP-MS, i.e. the digestion solution may be analysed without any further sample preparation. By using CV- AAS and CV-AFS, the Hg is reduced to its elemental state before it is analysed.

7.4.2 Wet digestion (digestion of electronics)

Wet digestion is recommended for the digestion of metals and electronics, with the exception of metals containing significant amounts of Si, Zr, Hf, Ti, Ta, Nb or W. For these materials and for polymers, microwave digestion, as described in 7.4.3, is recommended.

a) A sample of approximately 1 g is weighed into the reaction vessel and 30 ml concentrated nitric acid (7.3.b) is added. (When the available sample amount is 500 mg or less, follow the instructions given in 7.4.3).

   The vessel is equipped with a reflux cooler and an absorption vessel (on top of the reflux cooler - see Figure E.1 in Annex E) containing 10 ml of 0,5 mol/l nitric acid (7.3 d). Then a temperature program is started to digest the samples for 1 h at room temperature and for 2 h at 90 °C.

   After cooling to room temperature, the contents of the absorption tube are placed in the reaction vessel and the solution obtained is transferred to a 250 ml volumetric flask and filled with 5 % (m/m) nitric acid (7.3.g) to the mark (if the sample is digested completely).

b) For ICP-OES and ICP-MS measurements, the sample solution obtained may be diluted with water (7.3.a) to the appropriate concentration levels for measurements. Add 250 µl of internal standard (7.3.o) for a volume of 250 ml before filling to the mark.

c) If the sample is not completely digested (e.g. printed wiring boards), the sample is filtered with a filter (7.2.c) and the solid residue is washed four times with 15 ml of 5 % (m/m) nitric acid (7.3.g). The solution obtained is transferred to a 250 ml volumetric flask and filled with 5 % (m/m) nitric acid (7.3.g) to the mark.

d) Any sample residues shall be separated by a centrifuge or a filter. The residues shall be tested by appropriate measurements (e.g. XRF) to confirm the absence of target elements.

7.4.3 Microwave digestion

Microwave digestion is recommended for the following materials:

- Metals containing significant amounts of Si, Zr, Hf, Ti, Ta, Nb or W.
- Polymers.
- In cases where the available sample amount is smaller than 0,5 g.

NOTE 1 It is highly recommended that the same sample amounts and the same type of samples be weighed in one digestion run.

NOTE 2 Hg can be determined in the same solution with Pb and Cd obtained in a closed system for acid decomposition described in Clauses 8 to 10.

a) Weigh about 100 mg of the material into a PTFE-TFM or PFA-TFM vessel. Add 5 ml of concentrated nitric acid (7.3.b), 1,5 ml 50 % (m/m) HBF_4 solution (7.3.h), 1,5 ml 30 % (m/m) H_2O_2 (7.3.i) and 1 ml water (7.3.a). Close the vessel and digest the sample in the microwave oven following a digestion program specified in advance. An example of a suitable microwave program is given in Annex E.

b) After cooling the vessel to room temperature (approximate required time: 1 h), it is opened and the solution is filtered with filter (7.2.e) into a 25 ml flask, washed and filled to the mark with water (7.2.a).

c) Any sample residues shall be separated by a centrifuge or filter. The residues shall be checked by appropriate measurements (e.g. XRF) to confirm the absence of target elements.

NOTE 3 If HBF_4 is not available in sufficient purity, HF may be used as an alternative.

7.4.4 Preparation of laboratory reagent blank

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

7.5 Test procedure

7.5.1 Preparation of calibrant solutions

All analyses require that a calibration curve be prepared to cover the appropriate concentration range. Calibrants are prepared by diluting the stock metal solution (7.3.j) with

1,5 % (m/m) nitric acid (7.3.f). When internal standard methods (ICP-OES and ICP-MS) are used, the appropriate amounts of solution for the internal standard solutions (7.3.o) are added.

Prepare a reagent blank of 1,5 % (m/m) nitric acid (7.3.f) and at least three calibrants in graduated amounts in the appropriate range of the linear part of the calibration curve.

Standards shall be stored in Hg-free plastic containers. The standard solution (7.3 j) is usually stable for at least a year, whereas standard solutions shall be prepared daily.

The stability of Hg standard solutions can be severely affected by adsorption on the walls of the storage vessel. Therefore, it is recommended that Hg standard solutions be stabilized by the addition of a few drops of 5 % (m/m) $KMnO_4$ (7.3.l) solution.

NOTE A 1 % (m/v) gold (Au) solution can also be used instead of potassium permanganate.

7.5.2 Development of the calibration curve

The spectrometers are prepared for quantification with a reagent blank and a minimum of three standards.

a) CV-AAS

- The readings for the absorbance of the target element Hg are determined. The calibration curve obtained shows the relationship between the absorbance of Hg and its concentration.
- The recommended wavelength and examples of workable instrument parameters are listed in Annex E.

b) CV-AFS

- The readings for the fluorescence intensity of the target element Hg are determined. The calibration curve obtained shows the relationship between the fluorescence intensity of Hg and its concentration.
- The recommended wavelength and examples of workable instrument parameters are listed in Annex E.

c) ICP-OES

- The readings for the emission intensity of the target element Hg and those of the internal standard are determined. The calibration curve obtained shows the relationship between the ratio of emission intensities of Hg and those of the internal standard to the concentration of Hg.
- The recommended wavelength for Hg and examples of workable instrument parameters are listed in Annex E.

d) ICP-MS

- The readings for the mass/charge (m/z) intensity of the target element Hg and those of the internal standard are determined. The calibration curve obtained shows the relationship between the ratio of the m/z of Hg and that of the internal standard, and the concentration of Hg.
- The recommended m/z ratios for Hg and examples of workable instrument parameters are listed in Annex E.

A straight-line regression curve with a correlation (R^2) not less than <0,998 shall be used for initial calibration. In the event the check standard result (e.g. standard substance, calibrant etc.) differs from the expected value by more than 20 %, the calibration and all samples in the sequence shall be re-measured.

7.5.3 Measurement of the sample

After development of the calibration curve, 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 with 1 % (m/m) nitric acid (7.3.e) to the range of the calibration curve and measured 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.

NOTE If the sample is diluted to the range of calibration, it should be ensured that the internal standard concentration in the diluted sample solution is adjusted to the standard solution.

7.5.4 Calculation

The concentration measured in 7.5.3 is the concentration of Hg in the sample solution. The concentration of Hg in the sample is calculated from the following equation:

$$c = \frac{(A_1 - A_2)}{m} \times V \qquad (2)$$

where

c is the concentration of Hg in the sample in μg/g;

A_1 is the concentration of Hg in the sample solution in mg/l;

A_2 is the concentration of Hg in the laboratory reagent blank in mg/l;

V is the total volume for the sample solution in ml which depends on

- the type of digestion carried out (250 ml for wet digestion, 25 ml for microwave digestion),
- the type of the particular series of dilutions used;

m is the measured quantity of the sample in g.

7.6 Evaluation of the method

Volunteer laboratories chosen by IEC TC111 WG3 participated in an international interlaboratory study (IIS2) to determine whether the procedures provided were yielding replicable (and reliable) results. To sum up, four certified reference materials were given to different laboratories to determine the Hg values. The ratio between the assigned (or certified) values and the determined values was between 90 % and 97 %. Detailed results are listed in Table 8. Remarks on the limits of detection and the limits of quantification are given in Clause 4.

Table 8 – Mean results and recovery rates of mercury obtained in the IIS2 study

Number	Sample description	Certified value of Hg mg/kg	Mean result of Hg mg/kg	Standard deviation mg/kg	Recovery rate %	Range of recovery rate %	Number of data sets used
IIS2-C10	EC 680 (polyethylene)	25,3	24,6	3,7	97	83 - 119	5 Three replicates each
IIS2-C11	EC 681 (polyethylene)	4,5	4,4	0,4	97	84 - 106	5 Three replicates each; one outlier eliminated
IIS2-C12	NMIJ CRM 8112-a (acrylonitrile butadiene styrene)	100	90	6	90	83 - 99	9 Three replicates each; three outliers eliminated
IIS2-C13	NMIJ CRM 8113-a (acrylonitrile butadiene styrene)	941,5	893,0	53	95	89 - 103	9 Three replicates each; three outliers eliminated
NOTE A data set was specified as an outlier when the recovery rate of the data set obtained was lower than 50 % or higher than 200 %.							

8 Determination of lead and cadmium in polymers by ICP-OES, ICP-MS and AAS

8.1 Overview

This clause specifies the procedure for the determination of elemental lead (Pb) and elemental cadmium (Cd) in polymers from electrotechnical products. Three methods are described (ICP-OES, ICP-MS and AAS) as well as several procedures for preparation of the chemical sample, i.e. the sample solution from which the most appropriate method of analysis can be selected by the experts.

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

The samples are pre-cut and/or milled to an appropriate size for the method selected according to the procedure described in Clause 5. 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 (see Clause 6). Finally, in the digestion solution obtained, Pb and Cd are determined by ICP-OES, ICP-MS or by AAS.

The analysis by ICP-OES, ICP-MS or AAS generally allows determination of the target elements with high precision (uncertainty in the low per cent range) and/or high sensitivity (down to the µg/kg level). There are some limitations: the procedure does not apply to materials containing polyfluorinated polymers because of their stability. If sulfuric acid must

be used in the analytical procedure, there is a risk of losing Pb, thus resulting in erroneously low values for this analyte. The use of appropriate, sophisticated equipment, i.e. a microwave digestion system is strongly advised. However, if the experts can ensure their suitability, simpler alternatives may be used, e.g. the addition of boric acid instead of using an HF-resistant sample holder. Frequently occurring spectral interferences are given in Table F.1.

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.

For the results of the evaluation of the methods see 8.6.

The work according to this standard involves the use of toxic and hazardous substances. Detailed warnings are given below.

8.2 Apparatus, equipment and materials

The following items shall be used for the analysis:

a) ICP-OES: equipment consisting of sample holder, plasma torch, spray chamber, nebulizer, optical unit, detector, system control and data output device.

b) ICP-MS: equipment consisting of sample holder, plasma torch, spray chamber, nebulizer, interface, mass separator unit, system control and data output device.

c) AAS: apparatus consisting of a sample holder, nebulizer/burner system with air/acetylene burner head, radiation source lamps, detector, data processor and control system.

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

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

f) Argon gas: gas with purity of over 99,99 % (v/v).

g) Acetylene gas: gas with purity of over 99,99 % (v/v).

h) Glassware: all glassware shall be cleaned with 10 % (m/m) nitric acid before use:

   1) Kjeldahl flask: 100 ml;

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

   3) Volumetric flasks: such as 50 ml, 100 ml, 200 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) Funnel;

   6) Watch glass;

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

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

k) PTFE/PFA equipment (polytetrafluoroethylene (PTFE)/perfluoro alkoxyl alkane resin (PFA): all equipment shall be cleaned with 10 % (m/m) nitric acid (8.3 d) before use:

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

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

l) Micropipettes: such as 10 µl, 100 µl, 200 µl, etc.

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

n) Containers made of high-density polyethylene (PE-HD) shall be used for ordinary measurement of element concentration. For determination at the ultra-trace level, containers made of perfluoro alkoxyl 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.

o) Electric hot plate or heated sand bath.

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

q) Bunsen burner or similar type of gas burner.

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

NOTE 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.

s) PTFE microwave digestion vessel: such as 100 ml, etc.

t) Heat-resistant thermal insulation board.

u) Paper filter.

8.3 Reagents

For the determination of elements at trace level, the reagent 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} % (m/m) in total.

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

b) Sulfuric acid: $\rho(H_2SO_4)$ = 1,84 g/ml, 95 % (m/m), “trace metal” grade.

c) Nitric acid: $\rho(HNO_3)$ = 1,40 g/ml, 65 % (m/m), “trace metal” grade.

d) Nitric acid, 10 % (m/m) (“trace metal” grade).

e) Hydrogen peroxide: $\rho(H_2O_2)$ = 1,10 g/ml, 30 % (m/m), “trace metal” grade.

f) Hydrochloric acid: ρ(HCl) = 1,19 g/ml, 37 % (m/m), “trace metal” grade.

g) Hydrofluoric acid: ρ(HF) = 1,18 g/ml, 40 % (m/m), “trace metal” grade.

h) Boric acid (HBO_3), 5 % (m/m) (50 mg/ml), “trace metal” grade.

i) Certified standard solution with 1 000 mg/kg of Pb.

j) Certified standard solution with 1 000 mg/kg of Cd.

k) Certified internal standard solution.

- Internal standard elements that do not interfere with the target element shall be used. Moreover, 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.
- For use with ICP-OES, Sc or Y is recommended, for use with ICP-MS, Rh is recommended. The concentration used shall be 1 000 mg/kg.

NOTE 1 The toxicity of each reagent listed under b) to j) 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.

NOTE 2 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.

NOTE 3 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.

NOTE 4 The exhaust gases from the plasma should be ducted away by an efficient fume extraction system.

NOTE 5 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.

8.4 Sample preparation

8.4.1 Test portion

The different analytical procedures which can be used as alternatives, according to this 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. Some general considerations about limitations and risks have been given in 8.1.

For acid digestion, 400 mg of sample that has been ground, milled or cut is measured accurately to the 0,1 mg level. For the dry ashing method, or for the closed system for acid decomposition, 200 mg of sample that has been ground, milled or cut is measured accurately to the 0,1 mg level.

8.4.2 Preparation of test solution

8.4.2.1 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 (8.2.j) mounted in the hole in the heat-resistant thermal insulation board (8.2.t).

b) Heat the crucible (8.2.j) gently with the burner (8.2.q) 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 (8.2.p) at 550 °C ± 25 °C[27], 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 (8.2.j) and its contents from the furnace (8.1.p) and allow to cool to ambient temperature.

g) Add 5 ml of nitric acid (8.3.c), transfer the resulting solution to a 50 ml volumetric flask (8.2.h.3) and fill with water (8.3.a) to the mark. This is the concentrate sample solution. Dilute the concentrate sample solution with water (8.3.a) to the appropriate concentration level for each measurement apparatus. If an internal standard (8.3.k) is to be used, it shall be added before filling. For a final volume of 50 ml, add 500 µl of internal standard (8.3.k) for ICP-OES and for ICP-MS (after a 1:1 000 dilution step) before filling.

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

1) Measure the sample into a crucible (8.2.j)

2) Add 5 ml to 15 ml of sulfuric acid (8.3.b) and heat the crucible (8.2.j) and its contents slowly on a hot plate or sand bath (8.2.o) until the plastic melts and blackens.

3) After cooling, add 5 ml of nitric acid (8.3.c) and continue heating until the plastic degrades completely and white fumes are generated.

4) After cooling, the crucible (8.2.j) is placed in a muffle furnace (8.2.p) maintained at 550 °C ± 25 °C and the sample is evaporated, dried and ashed until the carbon has been completely incinerated.

5) After ashing, add 5 ml of nitric acid (8.3.c) and transfer the resulting solution to a 50 ml volumetric flask (8.2.h.3) and fill with water (8.3.a) to the mark. The resulting solution is the concentrate sample solution. Dilute the concentrate sample solution with water (8.3.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 (8.3.k) for ICP-OES and ICP-MS (after a 1:1 000 dilution step) shall be added before filling.

6) Any sample residues shall be separated by a centrifuge or a filter. The residues shall be checked by appropriate measurements (e.g. XRF) to confirm the absence of target elements.

NOTE This method does not apply to fluorocarbons (see 8.1).

8.4.2.2 Acid digestion method

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

a) Measure the sample into a flask (8.2.h.1). Add 5 ml of sulfuric acid (8.3.b) and 1 ml of nitric acid (8.3.c) and heat the flask until the sample ashes and white fumes are generated. After heating is stopped, nitric acid (8.3.c) 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 (8.3.c) are repeated until the decomposed solution turns pale yellow.

b) Allow the sample to cool down for several minutes. Add hydrogen peroxide (8.3.e) 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 (8.2.h.3) and filled with water (8.3.a) to the mark. The resulting solution is the concentrate sample solution. Dilute the concentrate sample solution with water (8.3.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 (8.2.k) 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, TI etc. (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 (8.3.c) in small quantities (approximately 0,5 ml), and heat until white fumes are generated. The heating and decomposition with nitric acid (8.3.c) 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 a fluorocarbon resin vessel. Add 5 ml of HF (8.3.g) and heat the vessel until white fumes are generated. Add boric acid (8.3.h) 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 (8.2.k.2) and fill with water (8.3.a) to the mark. The resulting solution is the concentrate sample solution. Dilute the concentrate sample solution with water (8.3.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 (8.3.k) 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) to confirm the absence of target elements.

8.4.2.3 Closed system for acid decomposition

If a closed system is used, the following steps are carried out:

a) Measure the sample into a microwave digestion vessel and add 5 ml of nitric acid (8.3.c). Add hydrogen peroxide (8.3.e) 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 (8.2.r). Digest in the microwave oven following a decomposition program specified in advance. Cool the sample and transfer the solution to a 50 ml volumetric flask (8.2.h.3), which is then filled with water (8.3.a) to the mark. The resulting solution is the concentrate sample solution. Dilute the concentrate sample solution with water (8.3.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 (8.3 k) for ICP-OES, and ICP-MS (after a 1:1 000 dilution step) before filling.

NOTE 1 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, Ti etc. (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 (8.3.c) and 1 ml of HF (8.3.g). Add hydrogen peroxide (8.3.e) 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 (8.2.r). The sample is digested in the microwave oven following a decomposition program specified in advance. Add boric acid (8.2.h) 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 (8.2.k.2) and fill the flask with water (8.3.a) to the mark. The resulting solution is the concentrate sample solution. Dilute the concentrate sample solution may be diluted with water (8.3.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 (8.3.k) for ICP-OES and ICP-MS (after a 1: 1 000 dilution step) before filling.

NOTE 2 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.

c) Any sample residues shall be separated by a centrifuge or a filter. The residues shall be checked by appropriate measurements (e.g. XRF) to confirm the absence of target elements.

8.4.3 Preparation of laboratory reagent blank

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

8.5 Test procedure

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 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.

NOTE In all cases, the acid should also be adjusted to the concentration of the sample.

8.5.1 Preparation of 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 (8.2.h.3). Next, add each reagent, and in the case of the internal standard method, the appropriate amounts of solution for the internal standard solutions (8.3.k) to achieve reagent

concentrations identical to those present in the sample solution. The resulting solution is the mixed calibrant solution.

8.5.2 Development of the calibration curve

The spectrometers are prepared for quantification. Some of the solution obtained as described in 8.5.1 is nebulized into the argon plasma or the acetylene/air flame. A HF-resistant sample introduction system shall be used when the sample solution contains HF.

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 Table F.1.

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 F.2.

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 extrapolarion of the additions curve to zero absorbance.
   - The wavelengths shall be selected with regard to typical measurement wavelengths for elements given in Table F.3. If there is interference from co-present substances, the standard additions method should be applied.

A straight-line regression curve with a correlation (R^2) not less than <0,998 is required for initial calibration. If the check standard result (e.g. standard substance, calibration solution, etc.) differs from the expected value by more than 20 %, the calibration and all samples in the sequence shall be re-measured.

8.5.3 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.

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

8.5.4 Calculation

The concentration measured in 8.5.3 is the concentration of each element in the sample solution. The concentration of each element in the sample is calculated from the equation:

$$c = \frac{(A_1 - A_2)}{\mathrm{m}} \times V \qquad (3)$$

where

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

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

A_2 is the concentration of Pb or Cd 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.

8.6 Evaluation of the method

As described in detail in 4.5, the instrument detection limits are generally quite low (sometimes very low), but do not represent the true LODs of a methodology applied to the analysis of real samples. To overcome this somewhat theoretical approach (see 8.1), IEC TC111 WG3 carried out several international interlaboratory studies (IIS).

In these studies, CRMs, donated samples of known composition and actual samples were analysed according to the analytical procedures described in this clause. The results gave an overview of the practically achievable LODs and, even more importantly, the precision and accuracy of the analytical procedures in routine analytical work.

For the methods described in this clause, the IIS revealed that the precision and accuracy were always within ± 20 % for amounts of Pb and Cd above 10 mg/kg, regardless of the particular method or equipment selected.

9 Determination of lead and cadmium in metals by ICP-OES, ICP-MS and AAS

9.1 Overview

This clause specifies the procedure for the determination of lead (Pb) and cadmium (Cd) in metals from electrotechnical products. Three methods are described, namely ICP-OES, ICP-MS and AAS. The samples are digested with acids such as hydrochloric acid or nitric acid. The Pb and Cd in the solutions thus obtained are determined either by ICP-OES, ICP-MS or AAS. The detailed procedures depend on the matrix as well as on the presence of particular elements; these are also described. Procedures are given for unknown samples and for samples where screening methods have already indicated the qualitative composition.

The test procedures described in this clause are intended to provide the highest level of accuracy and precision for concentrations of the regulated substances, which range from 10 mg/kg for Pb and Cd for ICP-OES and AAS, and from 0,1 mg/kg for Pb and Cd for ICP-MS. The procedures are not limited to higher concentrations.

There are limitations and risks due to the solution step of the sample. Firstly, precipitation of the target or other elements may occur (risk of co-precipitation), in which case the residues have to be checked separately or dissolved by another method and then combined with the test sample solution. Secondly, evaporation of the sample solution may occur due to vigorous

chemical reactions, especially when watch glasses are used to cover the reaction volume. The use of appropriate, sophisticated equipment, i.e. a microwave digestion system, is strongly advised. However, if the experts can ensure their suitability, simple alternatives may be used. Detailed information is given in the clause.

The results of the evaluation of the precision, accuracy and LOD of the methods are summarized in 9.7.

The work according to this standard involves the use of toxic and hazardous substances. A detailed warning is given in the clause.

9.2 Apparatus, equipment and materials

The following items shall be used for the analysis:

a) ICP-OES: equipment consisting of sample holder, plasma torch, spray chamber, nebulizer, optical unit, detector, system control and data output device.

b) ICP-MS: equipment consisting of sample holder, plasma torch, spray chamber, nebulizer, interface, mass separator unit, system control and data output device.

c) AAS: apparatus consisting of a sample holder, nebulizer/burner system with air/acetylene burner head, radiation source lamps, detector, data processor and control system.

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

e) Glassware: all glassware shall be cleaned with 10 % (m/m) nitric acid before use:

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

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

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

   4) Watch glass.

f) Micropipettes: such as 200 µl, 500 µl, 1 000 µl, etc.

g) Poly(tetrafluoroethylene) (PTFE)/perfluoro alkoxyl alkane resin (PFA) equipment: all equipment shall be cleaned with 10 % (m/m) nitric acid before use:

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

   2) Covers for beakers;

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

h) Volumetric flasks made of high-density polyethylene: such as 100 ml, 200 ml, 500 ml, etc. Where appropriate, other types of volumetric equipment with acceptable precision and accuracy can be used as an alternative to volumetric flasks.

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

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

j) Electric hot plate or heated sand bath.

k) HF-resistant sample holder: sample holder of which the sample insertion section and torch have been treated for resistance to HF.

l) Argon gas: gas with purity of over 99,99 % (v/v).

m) Acetylene gas: gas with purity of over 99,99 % (v/v).

n) Paper filter.

9.3 Reagents

For the determination of elements at trace level, the reagent 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 total trace metals shall be less than 1×10^{-6} % (m/m).

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

b) Nitric acid: $\rho(HNO_3)$ = 1,40 g/ml, 65 % (m/m), “trace metal” grade.

c) Nitric acid: dilution (1:2): dilute 1 volume of concentrated nitric acid (9.3.b) with 2 volumes of water (9.3.a).

d) Fluoroboric acid: HBF_4, 50 % (m/m) “trace metal” grade.

e) Hydrogen peroxide: $\rho(H_20_2)$ = 1,10 g/ml, 30 % (m/m), “trace metal” grade.

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

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

h) Sulfuric acid: $\rho(H_2SO_4)$ = 1,84 g/ml, 95 % (m/m), “trace metal” grade.

i) Sulfuric acid: dilution (1:2): dilute 1 volume of concentrated sulfuric acid (9.3.h) with 2 volumes of water (9.3.a).

j) Hydrofluoric acid: ρ(HF) = 1,18 g/ml, 40 % (m/m), “trace metal” grade.

k) Hydrochloric acid: ρ(HCl) = 1,16 g/ml, 37 % (m/m), “trace metal” grade.

l) Hydrobromic acid: ρ(HBr) = 1,48 g/ml, 47 % to 49 % (m/m), “trace metal” grade.

m) Boric acid(HBO_3) 50 mg/ml, 5 % (m/m), “trace metal” grade.

n) Mixed acid 1 (two parts hydrochloric acid (9.3.k), one part nitric acid (9.3.b) and two parts water (9.3.a).

o) Mixed acid 2 (one part nitric acid (9.3.b) and three parts hydrofluoric acid (9.3.j).

p) Mixed acid 3 (three parts hydrochloric acid (9.3.k) and one part nitric acid (9.3.b).

q) Standard solution with 1 000 mg/l of Pb.

r) Standard solution with 1 000 mg/l of Cd.

s) Internal standard solution.

   Internal standard elements that do not interfere with the target element are used. The presence of these internal standard elements in the sample solution shall also be at negligible levels. Sc, In, Tb, Lu, Re, Rh, Bi and Y may be used as internal standard elements.

NOTE 1 The toxicity of each reagent used 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.

NOTE 2 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.

NOTE 3 Toxic fumes are released by nitric acid. Always carry out digestion in a fume cupboard and when adding acid to samples because of the possibility of toxic gases being released.

NOTE 4 The exhaust gases from the plasma should be ducted away by an efficient fume extraction system.

NOTE 5 Special precautionary measures should be taken when hydrofluoric acid or perchloric acid are used (a special hood is required due to the risk of explosion, and HF antidote gel (2,5 % calcium gluconate in a water soluble gel) for first aid treatment of HF burns of the skin).

9.4 Sample preparation

9.4.1 Test portion

1 g of sample is measured accurately to a 0,1 mg level and is placed in a glass beaker or a PTFE/PFA beaker (9.2.g.1) when using HF (9.3.j).

9.4.2 Preparation of the test sample solution

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.

a) Common methods of sample digestion

   A glass beaker (9.2.e.1) containing the sample is covered with a watch glass (9.2.e.4). Add 20 ml of mixed acid 1 (9.3.n) 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 (9.3.a). Transfer the solution to a 100 ml volumetric flask (9.2.e.2) and fill with water (9.3.a) to the mark. The resulting solution is the concentrate sample solution. Dilute the concentrate sample solution with water (9.3.a) to the appropriate concentration level for each measurement apparatus. If necessary, an internal standard solution (9.3.s), e.g. containing Rh is added before the flask (9.2.e.2) is filled with water (9.3.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) If the sample contains Zr, Hf, Ti, Ta, Nb or W

   A PTFE/PFA beaker (9.2.g.1) containing the sample is covered (9.2.g.2). 20 ml of mixed acid 2 (9.3.o) is added and the beaker (9.2.g.1) is heated until the sample is dissolved. After cooling to room temperature, the underside of the cover (9.2.g.2) and the inside wall of the beaker (9.2.g.1) are rinsed with water (9.3.a), and the cover (9.2.g.2) is removed. The solution is transferred to a 100 ml volumetric flask (9.2.g.3) and filled with water to the mark. The resulting solution is the concentrate sample solution. The concentrate sample solution is diluted with water (9.3.a) to the appropriate concentration level for each measurement apparatus. If necessary, an internal standard solution (9.3.s), e.g. containing Rh, is added before the flask (9.2.g.3) is filled with water (9.3.a) to the mark. As hydrofluoric acid (9.3.j) is used, the internal standard solution (9.3.s) 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.

c) If the sample contains Sn

   – A beaker (9.2.e.1) containing the sample is covered. 10 ml of mixed acid 3 (9.3.p) is added in small quantities. After the violent reaction ends, the beaker (9.2.e.1) is heated slowly until the sample is completely dissolved. After cooling, the underside of the cover and the inside wall of the beaker (9.2.e.1) are rinsed with water (9.3.a), and the cover is removed. 10 ml of sulfuric acid (9.3.h) is added and the beaker (9.3.e.1) is heated until white fumes of SO_3 are generated. After cooling for several minutes, 20 ml of hydrobromic acid (9.3.l) are added, and the beaker (9.2.e.1) is heated until white fumes become visible. This process is repeated three times. After cooling to room

temperature, 10 ml of nitric acid (9.3.b) is added to dissolve the salts. The solution is transferred to a 100 ml volumetric flask (9.2.e.2) which is then filled with water (9.3.a) to the mark. The resulting solution is the concentrate sample solution. The concentrate sample solution is diluted with water (9.3.a) to the appropriate concentration level for each measurement apparatus. If necessary, an internal standard solution (9.3.s), e.g. containing Rh, is added to the flask (9.2.e.2) before it is filled with water (9.3.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 (9.3.s) shall be documented in the test report.

– Alternatively, 1 g of sample is dissolved by the addition of 40 ml of water (9.3.a), 12 ml of nitric acid (9.3.b) and 6 ml of freshly prepared fluoroboric acid (9.3.d) (200 ml of 40 % (m/m) hydrofluoric acid (9.3.j) with 75 g of boric acid (9.3.m). A PTFE/PFA beaker (9.2.g.1) and a high-density polyethylene or PTFE/PFA volumetric flask (9.2.g.3) shall be used.

d) 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) to confirm the absence of target elements.

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

9.5 Preparation of laboratory reagent blank

A procedure which is identical to that for the preparation of the test sample solution is carried out concurrently but without the sample.

9.6 Test procedure

The calibration curve method is used for sample measurement. If the sample composition can be identified clearly, the calibration method (matrix matching method) is used. If it is unknown, the internal standard method (intensity comparison method) is used (not suitable for AAS). If required, the standard addition method may also be used.

NOTE 1 It is recommended that the matrix matching method be used for high matrix concentration samples. In all cases, the acid should also be adjusted to the sample concentration.

NOTE 2 If the matrix effect cannot be corrected, the matrix elements should be eliminated by means of a separation method such as solvent extraction, ion exchange, etc.

9.6.1 Preparation of the calibrant

Two different methods are used for the preparation of the calibrant.

a) Calibration method (matrix matching method)

– 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 (9.2.e.2). In the matrix matching method, a close matrix matching of the standard solution is necessary. In this case, the matrix elements shall either be known (e.g. from previously documented specifications) or have been evaluated by previous screening experiments using XRF. Each reagent and the matrix (elements) are added to prepare mixed calibrants that are equivalent to those of the sample solution.

– If hydrofluoric acid is used, a PTFE/PFA beaker (9.2.g.1) and a high-density polyethylene or PTFE/PFA volumetric flask (9.2.g.3) shall be used.

b) Internal standard method

– To achieve concentrations equivalent to the concentration of the sample solution, reagents and internal standard elements are added to prepare mixed calibrant solutions.

– If hydrofluoric acid is used, a PTFE/PFA beaker and a high-density polyethylene or PTFE/PFA volumetric flask shall be used.

9.6.2 Measurement of the calibrant

Measurement of the calibrant depends on the equipment used.

a) ICP-OES

– In ICP-OES, part of the calibration solutions prepared as described in 9.6.1 is introduced into the argon plasma under optimized conditions to measure the intensities of the atomic spectral lines of each target element. In the calibration method (matrix matching method), the curve showing the relationship between the intensities of the atomic spectral lines and concentration is developed as the calibration curve. In the internal standard method, the curve showing the relationship between the intensity ratio and the concentration of the target element with respect to the internal standard element is developed as the calibration curve.

– A hydrofluoric acid-resistant sample holder and torch shall be used if the solution contains hydrofluoric acid.

– The recommended wavelength is selected from the spectral lines for each element. The wavelength shall be selected with regard to typical measurement wavelengths for elements given in Table G.1. A thorough study of the limit of detection, measurement precision, etc. shall be made. If there is interference from co-present substances, either a wavelength that does not interfere with the calibration range shall be selected or adjustments shall be made to the intensity of interference using a suitable method.

b) ICP-MS

– The ICP-MS is prepared for quantification. Some of the solution obtained according to 9.6.1 is nebulized into the argon plasma through the sample holder. A hydrofluoric acid-resistant sample holder shall be used when the solution contains hydrofluoric acid. The readings for the m/z of the target elements and the internal standard element are determined, and the ratio of the reading for the target element to the reading for the internal standard element is calculated. The mass-charge ratios can be defined on the basis of the measured mass numbers shown in Table G.2.

c) AAS

– Portions of the calibration solutions, prepared as described in 9.6.1, are introduced into the air-acetylene flame in AAS under optimized conditions in order to measure the absorption of the wavelength of each target element. In the calibration method (matrix matching method), the curve showing the relationship between the absorption of the wavelength and the concentration is developed as the calibration curve.

– The wavelengths shall be selected with regard to typical measurement wavelengths for elements shown in Table G.3. In the case of interference from co-present substances, either a wavelength that does not interfere with the calibration range shall used or adjustments have to be made to the intensity of interference using a suitable method.

A straight-line regression curve with a correlation (R^2) not less than <0,998 shall be used for initial calibration. In the event that the check standard result (e.g. standard substance, calibrant etc.) differs from the expected value by more than 20 %, the calibration and all samples in the sequence shall be re-measured.

9.6.3 Measurement of the sample

After the calibration curve is developed, the calibration 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.

The measurement precision is checked with standard substances, calibration solutions, etc. at regular intervals (such as once every 10 samples). If necessary, a calibration curve shall be developed again.

NOTE If the sample is diluted to the range of calibration, it should be ensured that the internal standard concentration in the diluted sample solution is adjusted to the standard solution.

9.6.4 Calculation

The spectrometer readings of each sample obtained according to 9.6.3 and the calibration curve developed as described in 9.6.2 are employed to determine the net spectral intensity of each target element. The content rate of each element in the sample is calculated by the following equation:

$$c = \frac{(A_1 - A_2)}{m} \times V \quad (4)$$

where

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

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

A_2 is the concentration of Pb or Cd 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.

9.7 Evaluation of the method

As described in detail in 4.5, instrument detection limits are generally quite low (sometimes very low), but do not represent the true LODs of a methodology applied to the analysis of real samples. In order to overcome this somewhat theoretical approach (see 9.1), IEC TC 111 WG3 carried out several international interlaboratory studies (IIS).

In these studies, CRMs, donated samples of known composition and actual samples were analysed according to the analytical procedures described in this clause. The result gave an overview of the practically achievable LODs, and even more importantly, of the precision and accuracy of the analytical procedures in routine analytical work.

For the methods described in this clause, the IIS revealed that precision and accuracy were always within ± 20 % for amounts of Pb and Cd above 10 mg/kg, regardless of the particular method or equipment chosen.

10 Determination of lead and cadmium in electronics by ICP-OES, ICP-MS and AAS

10.1 Overview

This clause specifies the procedure for the determination of lead (Pb) and cadmium (Cd) in electronics (printed wiring boards or single components from electrical and electronic equipment). Three methods (ICP-OES, ICP-MS and AAS) and several procedures for preparing the sample solution are described, from which the most appropriate method of analysis can be selected by the experts.

The samples for analysis shall be available as ground material of those electronic products described in Clause 5. 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 and Cd are determined either simultaneously in the digestion solution by ICP-OES or by ICP-MS or one element after the other is determined by AAS.

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

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

Analyses by ICP-OES, ICP-MS or AAS generally allow the determination of the target elements with high precision (uncertainty in the low percent range) and/or high sensitivity. The advantages of these methods may be limited when the samples to be analysed have a highly complex composition. Samples shall be destroyed by appropriate mechanical means prior to chemical digestion. The correct particle size as a function of the amount of starting material is essential. In order to fulfil the minimum requirements for a correct analysis, the maximum particle size and minimum amounts of sample are given in this clause. It is highly likely that after the digestion methods have been carried out that 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. This standard strongly recommends the use of sophisticated equipment, e.g. a microwave digestion system for the digestion methods. Nevertheless, if the user can ensure the suitability of a simpler approach, it may be applied. Any deviation from the described procedures shall be evaluated and documented in the test report.

For the results of the evaluation of precision, accuracy and LOD of the methods described in this clause, see 10.6.

The work described in this standard involves the use of toxic and hazardous substances. A detailed warning is given.

10.2 Apparatus, equipment and materials

The following items shall be used for the analysis:

a) ICP-OES: equipment consisting of sample holder, plasma torch, spray chamber, nebulizer, optical unit, detector, system control and data output device.

b) ICP-MS: equipment consisting of sample holder, plasma torch, spray chamber, nebulizer, interface, mass separator unit, system control and data output device.

c) AAS: equipment consisting of a sample holder, nebulizer/burner system with air-acetylene burner head, radiation source lamps, detector, data processor and control system.

d) Hydrofluoric acid-resistant sample holder: sample holder into which the sample insertion section and torch are treated for resistance to hydrofluoric acid.

e) Argon gas: gas with a purity of over 99,99 % (v/v).

f) Acetylene gas: gas with purity of over 99,99 % (v/v).

g) 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.

h) Microwave digestion system: microwave sample preparation system equipped with a sample holder and high-pressure polytetrafluoroethylene/tetrafluoroethylene modified PTFE/TFM or perfluoro alkoxyl alkane resin/tetrafluoroethylene modified (PFA/TFM) or other vessels based on fluorocarbon materials with a capacity of 40 ml.

NOTE 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.

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

j) Glassware: all glassware shall be cleaned with 10 % (m/m) nitric acid (10.3.h) before use.

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

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

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

4) Graduated cylinder: such as 1 ml, 5 ml, 50 ml, etc.

5) Watch glass.

k) Micropipettes: such as 200 µl, 500 µl, 1 000 µl, etc.

l) PTFE/PFA containers: all equipment shall be cleaned with 10 % (m/m) nitric acid (10.3.h) before use.

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

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

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

Containers made of high-density polyethylene shall be used for ordinary measurement of element concentration. For determination at the ultra-trace level, containers made of perfluoro alkoxyl 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.

n) Electric hot plate or heated sand bath.

o) Microwave digestion vessel: such as 40 ml, 100 ml, etc.

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

10.3 Reagents

For the determination of elements at trace level, the reagent 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: total trace metals shall be less than 1×10^{-6} % (m/m).

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

b) Hydrochloric acid: ρ(HCl) = 1,16 g/ml, 37 % (m/m), “trace metal” grade.

c) Hydrochloric acid: dilution (1:2): one part hydrochloric acid (10.3.b) diluted with 2 parts water (10.3.a), “trace metal” grade.

d) Hydrochloric acid, 5 % (m/m), “trace metal” grade.

e) Hydrochloric acid, 10 % (m/m), “trace metal” grade.

f) Nitric acid: ρ(HNO_3) =1,40 g/ml, 65 % (m/m), “trace metal” grade.

g) Nitric acid, 0,5 mol/l, “trace metal” grade.

h) Nitric acid, 10 % (m/m), “trace metal” grade.

i) Mixed acid (3 parts hydrochloric acid (10.3.b) and 1 part nitric acid (10.3.f).

j) Fluoroboric acid: HBF_4, 50 % (m/m), “trace metal” grade.

k) Hydrogen peroxide H_2O_2, 30 % (m/m), “trace metal” grade.

l) Standard solution with 1 000 mg/kg of lead.

m) Standard solution with 1 000 mg/kg of cadmium.

n) Standard solution with 10 000 mg/kg of copper.

o) Standard solution with 10 000 mg/kg of iron.

p) Internal standard solution: internal standard elements that do not interfere with the target element shall be used. Furthermore, the presence of these internal standard elements in the sample solution shall be at a negligible level. Sc, In, Tb, Lu, Re, Rh, Bi and Y may be used as internal standard elements for the purpose of this specific spectrometry.

NOTE 1 The toxicity of each reagent used 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.

NOTE 2 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.

NOTE 3 Toxic fumes are released by nitric acid. Always carry out digestion in a fume cupboard and when adding acid to samples because of the possibility of toxic gases being released.

NOTE 4 The exhaust gases from the plasma should be ducted away by an efficient fume extraction system.

NOTE 5 Special precautionary measures should be taken when hydrofluoric acid or perchloric acid are used (a special hood is required due to the risk of explosion and HF antidote gel (2,5 % calcium gluconate in a water soluble gel) for first aid treatment of HF burns of the skin).

10.4 Sample preparation

The preparation of a test sample solution described here does not necessarily cover all electronics and their compounds. Generally, the preparation of a solution with HCl, HNO_3 or a mixture thereof is recommended. $HClO_4$, H_2SO_4, etc. shall be added as necessary to samples that are difficult to dissolve with HCl and HNO_3. Please keep in mind that the use of H_2SO_4 is critical in the determination of Pb due to the risk of losing some of the target element. Samples shall be completely dissolved without any residues under heating at high temperatures.

When dissolving metals or especially mixtures thereof with strong acids, there is always a risk of precipitation (e.g. Pb and Ba with H_2SO_4, Ag with HCl, and Al may form oxides/oxide-hydrates and the like). Although these elements are often not covered by legislation, there is the risk of loss of the target element due to co-precipitation. For this clause it has to be ensured that no target elements are lost in the test sample solution. Any residues must either be checked by a different method to determine whether they contain target elements, or after acid dissolution the residues must be dissolved completely by further dissolution methods (such as alkali fusion or the use of an air-tight pressurised vessel). The residues that have been treated in this way are then combined with the acid-dissolved solution and the measurement procedure is carried out.

10.4.1 Test portion

The different analytical procedures which can be used alternatively according to this clause need different amounts of sample to achieve the required quality of results. In the case of electronics, the sample shall first be destroyed mechanically by appropriate means (e.g. grinding, milling, mill-cutting) before chemical digestion of the powder can start. In order to ensure a representative sample-taking at this step, a certain particle size as a function of the starting amount of sample is required (see corresponding standard for sample preparation). The resulting concentrated solutions may be used directly in ICP-OES or AAS or can be diluted for use in ICP-MS.

10.4.2 Digestion with aqua regia

Approximately 2 g of the ground sample (maximum particle size: 250 µm) are weighed into the reaction vessel and 22,5 ml HCl (10.3.b) and 7,5 ml HNO_3 (10.3.f) are added. The vessel is equipped with a reflux cooler and an absorption vessel containing 10 ml 0,5 mol/l HNO_3 (10.3.g). 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 (10.2.p) and the solid residue is washed four times with 15 ml 5 % (m/m) HCl (10.3.d). The solution obtained is transferred to a 250 ml volumetric flask (10.2. j.2) and filled with 5 % (m/m) HCl (10.3.d) to the mark.

The resulting solution is the concentrate sample solution. The concentrate sample solution may be diluted with water to the appropriate concentration level for each measurement apparatus. If an internal standard is used, it must 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.

If there are sample residues on the filter, they shall be checked by appropriate measurements (e.g. XRF) to confirm the absence of target elements.

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 (10.2.j.1) containing the sample is covered with a watch glass (10.2.j.5). Mixed acid (10.3. i) is added and the beaker (10.2.j.1) 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 (10.2.j.5) and inside wall of the beaker (10.2.j.1) are rinsed with water (10.3.a), and the watch glass (10.2.j.5) is removed. After cooling, the sample is filtered with a 0,45 µm glass microfibre filter (10.2.p). The residues are rinsed with 5 % (m/m) HCl (10.3.d). The solution is transferred to a volumetric flask (10.2.j.2) and filled with water (10.3.a) to the mark. The resulting solution is used for further measurements.

10.4.3 Microwave digestion

200 mg of ground sample (maximum particle size: 250 µm) is weighed into a PTFE/TFM, a PTFE/PFA or a vessel made from another fluorocarbon material (10.2.l). 4 ml of HNO_3 (10.3.f), 2 ml of HBF_4 (10.3.j), 1 ml of H_2O_2 (10.2.k) and 1 ml of water (10.3.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 (10.2.h) 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.

The vessel is opened after cooling to room temperature (approximate time required: 1 h), and 4 ml HCl (10.3.b) are added. After sealing the vessel again, further elements are dissolved with HCl (10.3.b) during a second microwave-enhanced digestion step (step B). An example of a suitable microwave program (steps A and B) is given in Table H.1.

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 (10.2 p) into a 25 ml flask (10.2.j.2), washed and filled to the mark with 5 % (m/m) HCl (10.3.d). If there are sample residues on the filter, they must be checked by appropriate measurements (e.g. XRF) to confirm the absence of target elements.

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.

NOTE 2 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.

NOTE 3 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 (10.2.p) into a 100 ml volumetric flask (10.2.j.2), washed and the flask is filled to the mark with 5 % (m/m) HCl (10.3.d).

If there are sample residues on the filter, they shall be checked by appropriate measurements (e.g. XRF) to confirm the absence of target elements.

10.5 Test procedure

The calibration curve method is used for sample measurement. Electronics (PWBs, single components) are samples with a complex matrix for the analytical methods in this clause, even after sample preparation. After digestion (aqua regia or microwave), the solutions have, for example, high concentrations of copper, iron and so forth. If the sample composition can be identified clearly, the calibration method (matrix matching method) is used for ICP-OES and AAS. The internal standard method (intensity comparison method) is recommended for ICP-MS.

NOTE 1 To increase the reliability of the test method, the standard-addition method may be used.

NOTE 2 If the matrix effect cannot be corrected, the matrix elements should be eliminated by means of a separation method such as solvent extraction, ion exchange, etc.

10.5.1 Preparation of a calibrant solution

Two different methods are used for the preparation of a calibrant solution.

a) Calibration method (matrix matching method)
   - After gradually diluting each standard element solution, the diluted standard solutions containing 0 µg to 100 µg of each element are transferred to 100 ml volumetric flasks (10.2.j.2). For the matrix matching method, a close matrix matching of standard solution is required. The matrix elements are identified by previous XRF screening. In order to achieve an equivalent to that of the sample solution, reagent and matrix elements are added to prepare mixed calibrant solutions. The resulting solution is the mixed calibration solution.
   - If HBF_4 is used, a high-density polyethylene volumetric flask or a PTFE/PFA volumetric flask (10.2.l.2) shall be used.

b) Internal standard method
   - To achieve concentrations equivalent to that of the sample solution, reagents and internal standard elements are added to prepare mixed calibrant solutions.
   - If HBF_4 is used, a high-density polyethylene volumetric flask or a PTFE/PFA volumetric flask (10.2.l.2) shall be used.

c) ICP-OES and AAS: The high iron and copper content requires a close matrix matching of standard solutions and an appropriate line selection. Therefore the calibration shall be carried out using matrix adjusted calibration solutions. Recommended wavelengths are listed in Table H.2.

d) ICP-MS: Here the use of an appropriate internal standard is recommended. Table H.3 gives the recommended m/z for the measurements together with potential interferences.

10.5.2 Standard preparation

Standard preparation depends on the equipment used.

a) ICP-OES and AAS
   - Sample solutions obtained from aqua regia digestion have a different matrix composition to solutions obtained by microwave digestion. Therefore different matrix matching for calibration is necessary. Standards prepared for ICP-OES can also be used for AAS measurement as long as target element concentrations of Pb and Cd are

in the linear range. A calibration blank and four calibrants are prepared as calibration solutions.

– Aqua regia digestion standards
  - Calibration blank: 100 ml 10 % (m/m) HCl (10.3.e).
  - Calibrants 1 to 3 (100 ml in each case): Solutions containing 1 500 µg/ml Fe and 1 500 µg/ml Cu, 24 ml HCl (10.3.b) and target elements Pb and Cd in different concentrations. 1,0 µg/ml target element in solution corresponds to 125 µg/g target element in electronics.
– Microwave digestion standards
  - Calibration blank: Mixture of 92 ml 10 % (m/m) HCl (10.3.e) and 8 ml HBF_4 50 % (m/m) (10.3.j).
  - Calibrants 1 to 3 (100 ml in each case): solutions containing 1 500 mg/l Fe and 1 500 mg/ml Cu, 24 ml HCl (10.3.e), 8 ml HBF_4 50 % (m/m) (10.3.j) and Pb and Cd in different concentrations. 1,2 µg/g target element in solution corresponds to 100 µg/g target element in electronics.

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

b) ICP-MS
  – Calibration blank and three calibrants are prepared as calibration solutions.
  – After gradually diluting each standard element solution, the solutions are transferred to 100 ml volumetric flasks (10.2.j.2) with 0 µg to 5 µg of each element. Next, each reagent and 1 µg of Rh are added to achieve reagent concentrations identical to that of the sample solution, and the mixed calibrant solution is prepared.

10.5.3 Calibration

Calibration depends on the equipment used.

a) ICP-OES and AAS
  – The calibration blank and standard solutions are measured by ICP-OES or AAS and linear calibration plots for Pb and Cd are set up.

b) ICP-MS
  – The ICP mass spectrometer is prepared for quantification. Some of the solution obtained in 10.5.1 is nebulized into the argon plasma through the sample holder. The readings for the m/z of the target elements and Rh are determined, and the ratio of the reading for the target element and the reading for the Rh is calculated.
  – The hydrofluoric acid-resistant sample introduction system shall be used when the sample contains HBF_4 or HF.

10.5.4 Development of the calibration curve

Development of the curve depends on the equipment used.

a) ICP-OES
  – A part of the calibration solutions prepared as described in 10.5.1 is introduced into the argon plasma in ICP-OES under optimized conditions to measure the intensities of the atomic spectra lines of each target element. In the calibration method (matrix matching method), the curve showing the relationship between the intensities of the atomic spectra lines and the concentration is developed as the calibration curve. In the internal standard method, the curve showing the relationship between the intensity ratio and the concentration of the target element with respect to the internal standard element is developed as the calibration curve.
  – A hydrofluoric acid-resistant sample introduction system and torch shall be used when the solution contains hydrofluoric acid.

- The recommended wavelength is selected from the spectral lines for each element. The wavelength shall be selected with regard to typical measurement wavelengths for the elements shown in Table H.2. A thorough study of the limit of detection, measurement precision, etc. shall be conducted. In the case of interference from co-present substances, either a wavelength that does not interfere with the calibration range shall be selected or adjustments have to be made to the intensity of interference using a suitable method.

b) ICP-MS

- The ICP-MS is prepared for quantification. Some of the solution obtained in 10.5.1 is nebulized into the argon plasma through the sample holder. A hydrofluoric acid-resistant sample holder shall be used when the solution contains hydrofluoric acid. The readings for the m/z of the target elements and the internal standard element are determined, and the ratio of the reading for the target element and the reading for the internal standard element is calculated. The mass-charge ratios may be defined on the basis of the measured mass numbers listed in Annex H.

c) AAS

- Portions of the calibration solutions prepared as described in 10.5.1 are introduced into the air-acetylene flame in the AAS under optimized conditions to measure the absorption of the wavelength of each target element. In the calibration method (matrix matching method), the curve showing the relationship between the absorption of the wavelength and the concentration is developed as the calibration curve.
- The wavelengths shall be selected with regard to typical measurement wavelengths for elements shown in Table H.4. In case of interference from co-present substances, either a wavelength that does not interfere with the calibration range has to be used or adjustments have to be made to the intensity of interference using a suitable method.

10.5.5 Measurement of the sample

After the calibration curve has been plotted, the calibration blank and the sample solution are measured. If the sample concentration is higher than that of the calibration curve, the solution shall be diluted to the range of the calibration curve and measured once again.

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

A straight-line regression curve with a correlation (R^2) not less than <0,998 shall be used for initial calibration. 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.

10.5.6 Calculation

The spectrometer readings of each sample obtained according to 10.5.3 and the calibration curve developed as described in 10.5.4 are used to determine the net spectral intensity of each target element. The content rate of each element in the sample is calculated by the following equation:

$$c = \frac{(A_1 - A_2)}{m} \times V \qquad (5)$$

where

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

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

A_2 is the concentration of Pb or Cd 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.

NOTE Due to the potential variation in analytical methods according to this clause, allowing individual dilutions of the starting test sample solution, Equation (5) only gives the general approach. It must be assured individually that all dilutions have been taken into account in the calculation of the result.

10.6 Evaluation of the method

As described in detail in 4.5 instrument detection limits are generally quite low (sometimes very low), but do not represent the true LODs of a methodology applied to the analysis of real samples. In order to overcome this somewhat theoretical approach (see 10.1), IEC TC111 WG3 carried out several international interlaboratory studies (IIS).

In these studies, CRMs, donated samples of known composition and real samples were analysed according to the analytical procedures described in this clause. The result gave an overview of the practically achievable LODs, and – even more important – of the precision and accuracy of the analytical procedures in routine analytical work.

For the methods described in this clause, very few samples were available. A precise statistical evaluation of accuracy, precision and LOD could not be done. The IIS revealed that, similar to Clauses 8 and 9, ± 20 % for precision and accuracy is a good estimate for amounts of Pb and Cd above 10 mg/kg, regardless of the particular method or equipment chosen.

Annex A
(informative)

Determination of PBB and PBDE in polymers by GC-MS

A.1 Introductory remark

This annex specifies a gas chromatography-mass spectrometry (GC-MS) test method for the determination of monobrominated to decabrominated biphenyls (PBB) and monobrominated to decabrominated diphenyl ethers (PBDE) in polymers of electrotechnical products having PBB and PBDE contents in the range of 100 mg/kg to 2 000 mg/kg and as high as 100 000 mg/kg for decaBDE.

This test method has been evaluated for PS-HI (polystyrene, high-impact), (PC+ABS) (a blend of polycarbonate and acrylonitrile butadiene styrene) and ABS (acrylonitrile butadiene styrene). The use of this method for other types or concentration ranges outside those specified above has not been evaluated.

PBB and PBDE compounds are determined using Soxhlet extraction of the polymers with separation by gas chromatography-mass spectrometry (GC-MS) qualitatively and quantitatively using single (or “selected”) ion monitoring (SIM).

A.2 Apparatus, equipment and materials

A.2.1 Apparatus

The following items shall be used for the analysis:

a) Analytical balance capable of measuring accurately to 0,000 1 g.
b) 1 ml, 5 ml, 10 ml, 100 ml volumetric flasks.
c) Soxhlet extractors:
   – 30 ml Soxhlet extractors;
   – 100 ml round-bottomed flask;
   – ground-in stopper NS 29/32;
   – Dimroth condenser NS 29/32;
   – boiling stones (e.g. glass pearls or Raschig rings).
d) Extraction thimble (cellulose, 30 ml, ID 22 mm, height 80 mm).
e) Glass wool (for extraction thimble).
f) Deactivated injector liner (for GC-MS).
g) Heating jackets.
h) Funnel.
i) Aluminium foil.
j) Cork rings.
k) Microlitre syringe or automatic pipettes.
l) Pasteur pipette.
m) 1,5 ml sample vials with 100 µl glass insert and a screw cap with polytetrafluoroethylene (PTFE) gasket or, depending on the analytical system, a comparable sample receptacle.
n) Mini-shaker (also known as vortexer or vortex mixer).

A.2.2 Equipment

A gas chromatograph with a capillary column coupled to a mass spectrometric detector (electron ionization, EI) is used for the analysis. The mass spectrometric detector shall be able to perform selective ion monitoring and have an upper mass range of at least 1 000 m/z. The high-range mass is required to unambiguously identify decaBDE and nonaBDE. The use of an autosampler is strongly recommended to ensure repeatability.

A column length of approximately 15 m has sufficient separation efficiency for PBB and PBDE compounds.

A.3 Reagents

All chemicals shall be tested for contamination and blank values prior to application.

a) Toluene (GC grade or higher).

b) Helium (purity of greater than 99,999 % (v/v)).

c) Technical BDE-209 with BDE-209 ~ 96,9 % and BDE-206 ~ 1,5 % solution.

d) PBB and PBDE calibrants (see Clause A.10).

e) Surrogate and internal standards:

   – Surrogate standard used to monitor analyte recovery according to A.5.1, A.5.3, A.6.1, A.6.2 and Clause A.8, e.g. DBOFB (4, 4'-dibromoctafluorobiphenyl) (n) or ^{13}C-labelled pentaBDE or octaBDE standard.

   – Internal standard used to correct for injection errors, according to A.5.1, A.5.4, A.6.2, and Clause A.8, e.g. CB209 (2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl).

NOTE 1 The standards are acceptable when using a quadrupole-type mass spectrometer. A high-resolution mass spectrometer will require the use of other suitable standard substances having a mass and elution time similar to that of the analyte. ^{13}C-labelled nonaBDE and ^{13}C-labelled decaBDE are recommended for the high-mass PBDEs.

NOTE 2 The standards suggested are adequate for measuring the concentrations of mono- through octaBDE. Due to their low mass and "high" volatility, these standards may be inadequate for measuring decaBDE and nonaBDE concentrations. By far the best calibration standard for these specific analytes would be ^{13}C-labelled decaBDE or one of the ^{13}C-labelled nonaBDEs. Some laboratories, operating on the principal of high volume/low price, may find these labelled materials too expensive for their business plan. A potential low-cost substitute is decaBB (BB 209). BB 209 has a high mass (943,1 g/mol vs. 959,1g/mol for decaBDE or 864,2 g/mol for nonaBDE), which elutes just before the three nonaBDEs on a typical DB-5 column. The presence of significant quantities of decaBB in the sample itself can readily be determined by monitoring the peak area of this standard, and comparing it to what is expected from the added quantity of decaBB. The use of the suggested labelled standards or decaBB should be limited to those analyses where the only analytes of interest are decaBDE and/or the nonaBDEs. With additional experimentation it may be possible to identify alternate standards that have the high mass and low volatility necessary for the quantification of the nonaBDEs and decaBDE.

A.4 General instructions for the analysis

The following general instructions shall be followed:

a) In order to reduce blank values, ensure the cleanliness of all glass equipment (excluding volumetric flasks) and deactivate glass wool (A.2.1.e) at 450 °C for at least 30 min. To avoid decomposition (debromination) of PBDEs by UV light during extraction and analysis, glass equipment made from brown glass shall be used, if possible. If no brown glass is available, aluminium foil can be used for protection from light.

b) If the amount of Br determined by XRF is considerably above the 0,1 % range, it will be necessary to carry out the analysis using an adjusted sample size or by repeating the analysis using an extract that has been appropriately diluted prior to internal standard addition.

A.5 Sample preparation

The samples shall be ground to pass through a 500 μm sieve before extraction. Cryogenic grinding with LN_2 cooling is strongly recommended.

A.5.1 Stock solutions

The following stock solutions shall be prepared:

a) Surrogate standard (to monitor analyte recovery): 50 μg/ml in toluene (A.3.a) (e.g. DBOFB).

b) Internal standard (to correct for injection error): 10 μg/ml in toluene (A.3.a) (e.g. CB209).

c) Polybrominated biphenyl (PBB) solution: 50 μg/ml in an organic solvent.

d) Polybrominated diphenyl ether (PBDE) solution: 50 μg/ml in an organic solvent.

e) Matrix spiking solution: Containing a total of 4 calibration congener standards in toluene (A.3.a) or other appropriate solvent (see A.5.3) as indicated in Table A.1.

Table A.1 – Matrix spiking solution

Bromination	Number of PBDE congeners	Number of PBB congeners
Mono to penta	1	1
Hexa- to deca-	1	1

The addition of 1 ml of a matrix spiking solution containing each of the four congeners in a concentration of 10 μg/ml is suitable for delivery of the required 10 μg (see A.8.1.b) in the matrix spike sample.

A.5.2 Pre-extraction of the Soxhlet extractors

To clean the Soxhlet extractors (A.2.1.c), a 2 h pre-extraction is carried out with 70 ml of the appropriate solvent (see A.5.3). The washing solvent is discarded.

A.5.3 Sample extraction

The following steps shall be followed for sample extraction:

a) Transfer 100 mg ± 10 mg of the sample into the extraction thimbles (A.2.1.d). Record the mass to the nearest 0,1 mg.

Toluene (A.3 a) shall be used as the extraction solvent.

b) The sample is transferred through a funnel (A.2.1.h) into the extraction thimble (A.2.1.d). In order to ensure a quantitative transfer, the funnel (A.2.1.h) is rinsed with approximately 10 ml of solvent.

c) 200 μl of the surrogate standard (A.5.1.a) (50 μg/ml) is added (in accordance with A.5.1).

d) In order to prevent the sample from floating, the thimble (A.2.1.d) is closed with glass wool (A.2.1.e). Approximately 60 ml of solvent is placed in the 100 ml round-bottomed flask (A.2.1.c), the equipment is covered with aluminium foil (A.2.1.i) to exclude light and the sample is extracted for at least 2 h with each cycle being approximately 2 min to 3 min. Shorter extraction times may result in lower recoveries of the analytes, particularly the higher molecular mass PBDEs.

e) The extract is placed in a 100 ml volumetric flask and the round-bottomed flask (A.2.1.c) is rinsed with approximately 5 ml of solvent.

NOTE If the solution exhibits turbidity due to the matrix, this can be reduced by adding 1 ml of methanol. The difference between the density of methanol and toluene (A.3.a) can be disregarded in this case in the calculation.

f) The volumetric flask is filled with 100 ml of solvent.

For a soluble polymer sample, the alternative extraction procedure may be applied as described in Clause A.11.

A.5.4 Addition of the internal standard (IS)

Prepare a 1 ml aliquot of each sample and standard to be analysed and place it in a 1 ml auto sampler vial. Add 20 µl of internal standard solution (A.5.1.b) to the vial and cap the vial. Invert the vial two times to mix.

Inject 1 µl of the sample solution into the GC-MS and analyse it according to the parameters described in Clause A.7.

A.6 Calibration

A calibration curve shall be developed for quantitative analysis. At least five calibration solutions shall be prepared in equidistant concentration steps. Quantification is made on the basis of the measurement of the peak areas. The linear regression fit of each calibration curve is required to have a relative standard deviation (RSD) of less than or equal to 15 % of the linear calibration function.

NOTE If the limiting value of the RSD of 15 % is exceeded, from the point of view of quality assurance, 2^{nd} order curve fitting does not guarantee any significantly better adjustment. Only statistical tests such as the F-test fulfil these requirements by comparing linear/2^{nd} order. That means that although the RSD value is exceeded, the calibration is linear.

A.6.1 PBB (1 µg/ml for each congener), PBDE (1 µg/ml for each congener) and surrogate standard (1 µg/ml) stock solution

100 µl of each PBB (A.5.1.c) and each PBDE (A.5.1.d) stock solution (50 µg/ml) and 100 µl of the surrogate stock solution (A.5.1.a) (50 µg/ml) is placed in a 5 ml volumetric flask (A.2.1.b) in accordance with A.5.1 and filled up with solvent up to the mark.

A.6.2 Calibration

The following calibration solutions are produced from the stock solution of the PBB (1 µg/ml for each congener), PBDE (1 µg/ml for each congener) and surrogate standard (0,2 µg/ml) (see A.6.1). The volumes indicated in Table A.2 are placed in a 1 ml volumetric flask (A.2.1.b) with a pipette and filled with solvent up to the mark, and then 20 µl of 10 µg/ml internal standard solution (A.5.1.b) is added.

NOTE For decaBDE, the calibration range suggested in Table A.2 may have to be modified. When establishing a calibration curve for decaBDE, the lower range should be set according to the instrument's sensitivity. A higher concentration may be used for the upper range to account for the generally high (10 % to 12 % (m/m)) levels of decaBDE normally found in samples.

Table A.2 – Calibration solutions of PBBs and PBDEs

No.	Volume **PBB+PBDE+ surrogate** µl (see A.6.1)	Volume **internal standard** µl (see A.5.1)	***c*(PBB)** ***c*(PBDE)** ng/ml per congener	***c*(Surrogate)** ng/ml
1	50	20	50	50
2	150	20	150	150
3	250	20	250	250
4	350	20	350	350
5	450	20	450	450

The internal standard is used for the correction of the injection error. Therefore the evaluation of the response factor or ratio is carried out by A/A_{IS}.

To produce the calibration straight lines the response A/A_{IS} is plotted against the concentration ratio c/c_{IS}.

A linear regression is carried out using Equation (A.1):

$$\frac{A}{A_{IS}} = a \times \frac{c}{c_{IS}} + b \tag{A.1}$$

where

A is the peak area of PBB, PBDE or the surrogate in the calibration solution;

A_{IS} is the peak area of the internal standard;

c is the concentration of PBB, PBDE or the surrogate per congener (ng/ml);

c_{IS} is the concentration of the internal standard (ng/ml).

NOTE 1 It is common practice to set the internal standard concentration to 1,00 ng/ml for the internal standard methods when the amount and concentration of internal standard added to the sample and calibrants prior to injection are the same.

a is the slope of the calibration curve;

b is the intercept on the y-axis of the calibration curve.

NOTE 2 A polynomial (e.g. second-order) regression may be utilized in the event that the relative standard deviation curve requirements cannot be achieved using linear regression. All quality control requirements are still in effect when using polynomial regression.

A.6.3 Calculation of PBB and PBDE concentration

Quantify the samples using the calibration curve. The instrument software usually performs the quantification. Normally, the calibration level of internal standard for all five calibration levels are set to 1 in the instrument method, but it can also be done manually using the equation of the fit from the calibration.

For a linear fit, the equation takes the form of:

$$y = ax + b \tag{A.2}$$

where

y is the response factor or ratio (A/A_{IS}) for the congener in the sample;

a is the slope of the line that best fits the calibration obtained in Equation (A.1);

x is the instrumental result (c/c_{IS} where c_{IS} is commonly = 1) in ng/ml (the concentration of the congener in the extract);

b is the y intercept or the concentration when the response factor equals 0, obtained from Equation (A.1);

For a quadratic fit the equation takes the form of:

$$y = ax^2 + bx + c \tag{A.3}$$

where

y is the response factor or ratio (A/A_{IS}) for the congener in the sample;

a and b are constants that correspond to the curve that best fits the calibration;

x is the instrumental result in ng/ml (the concentration of the congener in the extract);

c is the y intercept or the concentration when the response factor equals 0.

Equation (A.1), which is in the form of a linear equation, can be rewritten in the form of Equation (A.4):

$$c = \left(\frac{A}{A_{IS}} - b \right) \left(\frac{c_{IS}}{a} \right) \quad \text{(A.4)}$$

where

A is the peak area of PBB, PBDE or the surrogate;

A_{IS} is the peak area of the internal standard ;

c is the (intermediate) concentration of PBB, PBDE or the surrogate per congener in ng/ml;

c_{IS} is the concentration of the internal standard in ng/ml.

NOTE 1 It is common practice to set the internal standard concentration to 1,00 ng/ml for the internal standard methods when the amount and concentration of internal standard added to the sample and calibrants prior to injection are the same.

a is the slope of the calibration curve;

b is the intercept on the y-axis of the calibration curve.

NOTE 2 A polynomial (e.g. second-order) regression may be utilised in the event that the relative standard deviation curve requirements cannot be achieved using linear regression. All quality control requirements are still in effect when using polynomial regression.

If the concentration of each congener in a sample does not fall within the range of its respective calibrants, prepare a serial sample dilution that will bring the concentration of the congener to the midpoint of the calibration. Analyse the dilution and use the dilution factor to quantify the concentration of those congeners that were not within the calibration range in the original analysis. The dilution factor (D) can be calculated by dividing the final volume of the dilution by the volume of the aliquot:

$$D = \frac{V_f}{V_a} \quad \text{(A.5)}$$

where

D is the dilution factor;

V_f is the final volume in ml;

V_a is the volume of the aliquot in ml.

Equation (A.4) does not give the final concentration as the volume of the organic solvent, the mass of the sample and the volume of the extract and any dilution factor needs to be taken into account. A conversion factor (F) for the units from ng to µg is also needed. The final concentration of PBB, PBDE or the surrogate per congener in the sample can be calculated by using Equation (A 6):

$$c_{final} = \left(\frac{A}{A_{IS}} - b \right) \times \frac{c_{IS}}{a} \times \frac{V}{m} \times F \quad \text{(A.6)}$$

where

c_{final} is the concentration of PBB, PBDE or the surrogate per congener in the sample in µg/g;

V is the final extraction volume (100 ml);

m is the mass of the sample in grams;

F is a conversion factor for ng to µg (1×10^{-3}).

NOTE 3 Based on the experience of interlaboratory comparison, when calculating the PBDE concentrations in the sample, a potential blank value (according to 7.6.1.a) should be taken into account.

NOTE 4 The calculation shown above is for linear regression calibration only. A separate calculation is required if polynomial regression calibration is utilized.

The results are the sum of the concentration of each PBB (total PBBs) and the sum of the concentrations of each PBDE (total PBDEs).

The total PBDEs or the total PBBs can be calculated by summing the measured concentrations of all of the signals that meet the requirements for identification as a PBDE or PBB. The PBBs and the PBDEs that are included in the total shall include all the signals that meet the identification requirements (proper mass, appropriate retention time, correct ion ratios) for a PBB or a PBDE. The PBBs and PBDEs included in the totals shall not be limited only to those used in the calibration solutions since most entities are interested in the concentration of the total PBBs and total PBDEs, not specific isomers.

The calibration solutions can be used to establish an average response factor for each degree of bromination within the PBDEs and PBBs. The average response factors can then be used in the calculation of the measured concentration of detected congeners in the sample that are not included in the calibration (e.g. tentatively identified compounds or “TICS”, see also end of Clause A.7). Automatic integration of signals meeting the criteria for a PBB or a PBDE is a common function of software used in GC-MS trace analysis so the reporting of all PBBs and PBDEs in the totals is not a particularly onerous burden.

The PBDEs isolated from the sample extraction in A.5.3 are quantified by adding the internal standard (CB 209) (A.5.1.b) to an extract aliquot, injecting the solution into the GC-MS, measuring the area of the analyte peak(s) and the area of the CB 209 peak, and calculating the concentration of the analyte according to the formula given in A.6.3. Data on the surrogate standard (DBOFB) (A.5.1.a) are not used in the formula and are not used in any way to calculate the analyte concentration(s).

Only quantifiable values shall be summed. It is pointless to include limits of detection for concentrations of non-detected or non-quantifiable analytes, since these values would be so low as to render the numbers meaningless. In the event that there are no PBDEs or no PBBs detected in the sample, the total PBDE (or PBB) shall be reported as a function of the congener(s) with the highest method detection limits as determined in A.8.2. For example, if the method detection limit was 20 mg/kg for decaBB and 10 mg/kg for all other PBBs, and no PBBs were found in the sample, the total PBB is to be reported as <20 mg/kg.

It is important to remember that the measured concentration of decaBDE shall be reported separately from the total PBDEs since it is not a regulated substance and the determination of its concentration is solely for information purposes.

A.7 GC-MS

Different conditions might be necessary to optimize a specific GC-MS system to achieve effective separation of all calibration congeners and meet the QC and MDL requirements. The following parameters have been found suitable and are provided as an example:

a) GC column: non-polar (phenyl-arylene-polymer equivalent to 5 % phenyl-methyl-polysiloxane), length 15 m; internal diameter 0,25 mm; film thickness 0,1 µm. A high-temperature column (maximum = 400 °C) shall be used for the stated GC conditions in the method.

b) PTV, cool on-column, split/splitless injector or comparable injections systems can be used. The following parameters are recommended/optional:

   – PTV programme: 50 °C to 90 °C (0 min) at 300 °C/min to 350 °C (15 min); modus: splitless purge time 1 min; purge flow 50 ml/min.

NOTE 1 The initial temperature needs to be adjusted by the operator, depending on the boiling point of the solvent used.

NOTE 2 The use of an on-column injector can also be suggested as another means of introducing the sample. This may be particularly beneficial for the sensitivity of heavier congeners like octaBDE and nonaBDE. However, caution is advised due to sensitivity to matrix effects.

   – Split/splitless programme: 280 °C, 1,0 µl splitless, 0,5 min splitless time. Total flow = 54,2 ml/min at 0,5 min.

c) Injector liner: 4 mm single bottom taper glass liner with glass wool at bottom (deactivated).

NOTE 3 Additional deactivation of a purchased deactivated injector liner can be performed. This is especially important if the “PR-206” quality control requirements in Clause A.8 cannot be achieved. An example of a chemical deactivation procedure is as follows: take a commercially available, factory-deactivated liner (split/splitless single-taper with glass wool at the bottom) and immerse it in 5 % dimethyldichlorosilane (DMDCS) in dichloromethane or toluene (A.3.a) for 15 min. Pick it up with forceps and drain and immerse it three times in the DMDCS to make sure the glass wool has been thoroughly covered and flushed. Drain once more and blot the residue solution onto a clean wiper. Immerse the liner in methanol for 10 min to 15 min, and again drain/immerse three times. Rinse it inside and out with methanol from a squeeze bottle, followed by dichloromethane from a squeeze bottle. Transfer the liner to a vacuum oven purged with nitrogen and dry it at 110 °C for at least 15 min. Once dry it is ready for use.

d) Carrier: helium (A.3.b), 1,0 ml/min, constant flow.

e) Oven: 110 °C for 2 min, 40 °C/min ramp to 200 °C; 10 °C/min ramp to 260 °C; 20 °C/min ramp to 340 °C for 2 min.

f) Transfer line: 300 °C, direct.

g) Ion source temperature 230 °C.

h) Ionization method: electron ionization (EI), 70 eV.

i) Dwell time: 80 ms.

NOTE 4 To achieve the required data quality for a PBB or PBDE GC peak, it is recommended that 3 to 4 scans of the quantification ions selected be acquired per second. This will give the appropriate dwell time for each ion (m/z) to be monitored. The scan rate will result in a dwell time in the range of 80 ms per ion. It should be noted that by default some software sets the dwell time as a function of the scan rate. The analysis of PBBs and PBDEs is carried out in SIM (single ion monitoring) modus with the mass traces (the bold mass traces have been used for quantification) given in Tables A.3 and A.4. These have been found suitable and are provided as examples.

Table A.3 – Reference masses for the quantification of PBBs

	Ions (m/z)[a] monitored in the extract		
Mono-BB	**231,9**[b]	233,9	
Di-BB	309,8	**311,8**	313,8[c]
Tri-BB	387,8	**389,8**	391,8
Tetra-BB	307,8	**309,8**	467,7
Penta-BB	385,7	**387,7**	545,6
Hexa-BB	465,6	**467,6**	627,5
Hepta-BB	543,6	**545,6**	705,4
Octa-BB	623,5	**625,5**	627,5
Nona-BB	701,4	**703,4**	705,4 (863,4)
Deca-BB	781,3	**783,3**	785,3 (943,1;215,8, 382,6; 384,5)

[a] Brackets ( ) = optional ions.

[b] Bold = Quantification ions.

[c] Underlined = Identification ions.

Table A.4 – Reference masses for the quantification of PBDEs

	Ions (m/z)[a] monitored in the extract		
Mono-BDE	**247,9**	249,9	
Di-BDE	325,8	**327,8**	329,8[c]
Tri-BDE	403,8	**405,8**	407,8
Tetra-BDE	323,8	**325,8**	483,7
Penta-BDE	401,7	**403,7**	561,6
Hexa-BDE	481,6	**483,6**	643,.5
Hepta-BDE	559,6	**561,6**	721,4
Octa-BDE	639,5	**641,5**	643,5 (801,3)
Nona-BDE	717,4	**719,4**	721,4 (879,2)
Deca-BDE	797,3	**799,3**	959,1

[a] Brackets ( ) = optional ions.

[b] Bold = Quantification ions.

[c] Underlined = Identification ions.

A full scan run using a total ion current (“full scan”) MS method for each sample is also recommended for checking for the existence of peaks/congeners not present in the calibration (tentatively identified compounds or “TICS”) or not seen in the SIM window. If present, identify the peak and determine the class of compound (e.g. octabromobiphenyl, pentabromodiphenyl ether, etc.) by evaluation of the total ion spectra.

A.8 Quality control

At least annually (or any time instrumental parameters are changed), a 5 µg/ml solution of technical decaBDE (BDE-209, e.g. Wellington Laboratories Cat. # TBDE-83R or equivalent with BDE-209 ~ 96,9 % and BDE-206 ~ 1,5 %) with internal standard shall be analysed to confirm that the GC-MS system and parameters are suitable for the accurate determination of nonaBDEs in the presence of BDE-209 and to demonstrate that congener degradation is not

occurring. After the concentration (in µg/ml) of BDEs 206 and 209 measured in the injection solution is measured, the 206 / (206 + 209) per cent ratio ("PR – 206") is calculated as shown below.

$$PR = \frac{c_A}{c_A + c_B} \times 100 \quad \text{(A.7)}$$

where

PR is the per cent ratio, "PR-206";

c_A is the measured concentration of BDE-206 in µg/ml;

c_B is the measured concentration of BDE-209 in µg/ml

Table A.5 gives an example calculation.

Table A.5 – Example calculation

BDE congener	Theoretical injection concentration µg/ml	Measured concentration µg/ml	PR-206 %
BDE-209	4,845	5,200	(0,107 / 5,307) × 100 = 2,01
BDE-206	0,076	0,107	
Total		5,307	

A calculated PR-206 in the injection <4,0 is acceptable and samples can be tested. A calculated PR-206 >4,0 is unacceptable and samples are not to be tested until this condition is corrected. Effective corrections include replacement of the injection liner, reduction of the injection temperature, reduction of oven temperature or times, etc. New MDL studies are required if the instrumental parameters are changed.

A.8.1 Quality control method

The following steps are taken for the quality control:

a) One reagent blank shall be extracted with each sequence of samples. The reagent blank is 60 ml of only solvent taken through the entire extraction procedure according to A.5.3 or A.5.4.

b) One sample per sequence or one every ten samples, depending on the sample load, shall be spiked with 10 µg of each congener in the matrix spiking solution (see A.5.1.e). The following formula shall be used for calculation:

$$R = \frac{C_m - C}{C_s} \times 100 \quad \text{(A.8)}$$

where

R is the recovery of each PBB or PBDE congener in %;

c_m is the concentration of each PBB or PBDE congener in the matrix spike in ng/ml;

c is the concentration of each PBB or PBDE congener in the original sample in ng/ml;

C_s is the concentration of PBB or PBDE spike solution in ng/ml.

The per cent recovery for each congener shall be between 50 % and 150 %. The per cent recovery for each matrix spike shall be recorded and tracked in a spreadsheet to determine possible matrix effects in the analysis.

c) After every tenth sample run and at the end of each sample set, analyse a continuing calibration check standard (CCC). A CCC is an unextracted mid-range calibrant that is analysed as a sample.. The per cent recovery for each congener shall be between 70 % and 130 %. If the per cent recovery for any congener in the CCC standard falls outside of this range, the CCC standard should be reinjected within 12 h. If the recovery is still out of range after re-injection of the CCC standard, the analysis is stopped and maintenance shall be performed on the system to return it to optimal operating conditions. All samples injected before the last successful CCC standard may be reported, but all samples after the failing CCC standard shall be re-analysed with a new calibration.

d) The surrogate recovery shall be monitored for each sample. Per cent (%) surrogate recovery can be calculated by the following:

$$SR = \frac{ms}{10\ \mu g} \times 100 \qquad \text{(A.9)}$$

where

SR is the surrogate recovery, as a percentage (%);

ms is the total mass μg of surrogate measured in the final sample solution.

Acceptable recovery shall be between 70 % and 130 %. If the surrogate recovery for any sample is outside of these limits, the sample shall be re-analysed. If, after re-analysis, the surrogate recovery is not within these limits, the sample shall be re-extracted and re-analysed.

e) From the results of the five calibrants (according to A.6.2, Table A.2), calculate the average response (peak area) for the internal standard. The internal standard (IS) response for each sample (according to A.5.4) shall be monitored throughout the analysis and compared to the average. If at any point in the analysis the IS response fluctuates below 50 % or above 150 % of the average, the sample is deemed out of control and shall be re-analysed. If the IS response is still out of range, check the results of the duplicate extract. If both are out of range and biased in the same direction, report data as suspect due to matrix effects.

f) Samples containing significant concentrations of decaBDE (BDE-209) will have BDE-206 as the dominant nonaBDE, but only trace amounts of the nonaBDE, BDE-208. These qualitative nonaBDE concentrations can be used as an indication of the proper operation of the GC-MS system. The observation that BDE-206 is not the dominant nonaBDE, or the observation that BDE-208 is present in more than trace quantities in relation to the other nonaBDEs, indicates that corrective action is needed to render the instrumentation suitable for the accurate determination of nonaBDEs in the presence of significant concentrations of decaBDE.

g) A solvent blank run between each injection is recommended in order to be certain that there is no analyte carry-over from sample to sample. This is particularly important when samples containing high levels of decaBDE and/or potentially interfering brominated flame retardants are analysed. Failure to determine that the instrument is free of contaminating analytes may result in falsely elevated results. It is recommended that the solvent shall contain a small amount of silylating agent (BSA, BSTFA) to maintain the inertness of the injector liner.

h) The retention time of analytes having an identification mass corresponding to BDE-209 and BDE-206 shall be within ± 20 s of the BDE-209 and BDE-206 standards used in the calibration solutions in order to be confirmed as being BDE-209 and/or BDE-206. Peaks eluting outside this range cannot be identified as BDE-209 and/or BDE-206. (Samples containing decaBDE will have BDE-206 as the dominant nonaBDE.) The use of retention times as a confirmation criterion is a widely accepted practice.

A.8.2 Method detection limit and reporting limit

A method detection limit (MDL) study shall be completed before conducting this testing and each time there is a significant change in the method or instrument type. MDLs are defined as the minimum concentration of a substance that can be measured and reported with 99 % confidence from which a qualitative detection of a sample is permissible in a given matrix

concerning the analyte. The MDL is obtained by calculating the standard deviation for a minimum of seven replicate analyses. The standard deviation is then multiplied by the Student's *t* value for the total number of replicates (n) for n-1 degrees of freedom.

NOTE 1 All analyses used to calculate an MDL should be consecutive.

a) Mill approximately 2 g of suitable polymer from a pure source known not to contain brominated flame retardants or other compounds that may interfere with the analysis (e.g. polyethylene material BCR-681 or other).

b) Weigh out 100 mg of the milled polymer and place it in a new extraction thimble (A.2.1.d). Repeat this step six more times.

c) Place the extraction thimble (A.2.1.d) in the Soxhlet extraction apparatus (A.2.1.c).

d) Spike the thimble (A.2.1.d) with 5 µg of each calibration congener approximating the concentration of the lowest concentration calibrant.

e) Use the procedure (extraction according to A.5.3 or A.5.4) to extract each of the samples. Analyse accordingly.

f) The per cent recovery of each congener shall be between 70 % and 130 %. If the recovery is above or below these limits, the analysis shall be repeated. If the recovery is outside of these limits a second time, the entire extraction and analysis procedure shall be repeated.

g) Each congener shall have a calculated MDL of less than or equal to 100 mg/kg. If the calculated MDL for any of the congeners is above these limits, the procedure, extraction and analysis shall be repeated for that congener(s).

h) The reporting limit for each congener shall be, at a minimum, three times the respective MDL. Unlike the MDL, which relates to detection only, the reporting limit is a concentration that can be accurately quantified for a given compound.

NOTE 2 If the required MDL cannot be met, a concentration step can be added to the extraction procedure. Since the concentration step will also increase the resin concentration in the extract, a clean-up step is also recommended for each sample. This will extend the life of the column and reduce the frequency of instrument maintenance. If the concentration and clean-up steps are used in the analysis, they should also be used for the MDL samples.

A.9 Evaluation of the method

The precision and accuracy of the methods, the method detection limit, the way how to ensure these qualities of data and the determination process will be updated here once the suitable amounts of data become available from volunteer laboratories chosen by IEC TC111 WG3.

A.10 PBB and PBDE calibrants

All brominated species from mono- to decabrominated biphenyl (PBB) and mono- to decabrominated diphenyl ether (PBDE) shall be included in the calibration. The availability of congener standards for a particular PBB or PBDE (e.g. pentaBDE) may vary from region to region. The following is an example list of typically available calibration congeners that have been found suitable for this analysis.

Table A.6 – Example list of commercially available calibration congeners considered suitable for this analysis

PBB[a]	Compound name
BB-003	4-Bromo biphenyl
BB-015	4,4'-Dibromo biphenyl
BB-029	2,4,5-Tribromo biphenyl
BB-049	2,2',4,5'-Tetrabromo biphenyl
BB-077	3,3',4,4'-Tetrabromo biphenyl
BB-103	2,2',4,5',6-Pentabromo biphenyl
BB-153	2,2',4,4',5,5'-Hexabromo biphenyl
BB-169	3,3',4,4',5,5'-Hexabromo biphenyl
Dow FR-250	Technical mixture of nonabromo biphenyl, octabromo biphenyl (80 %) and heptabromo biphenyl
BB-209	Decabromo biphenyl
PBDE[a]	**Compound name**
BDE-003	4-Bromo diphenyl ether
BDE-015	4,4'-Dibromo diphenyl ether
BDE-033	2',3,4-Tribromo diphenyl ether
BDE-028	2,4,4'-Tribromo diphenyl ether
BDE-047	2,2',4,4'-Tetrabromo diphenyl ether
BDE-099	2,2',4,4',5-Pentabromo diphenyl ether
BDE-100	2,2',4,4',6-Pentabromo diphenyl ether
BDE-153	2,2',4,4',5,5'-Hexabromo diphenyl ether
BDE-154	2,2',4,4',5,6'-Hexabromo diphenyl ether
BDE-183	2,2',3,4,4',5',6-Heptabromo diphenyl ether
BDE-203	2,2',3,4,4',5,5',6-Octabromo diphenyl ether
BDE-206	2,2',3,3',4,4',5,5',6-Nonabromo diphenyl ether
BDE-209	Decabromo diphenyl ether

[a] Ballschmiter and Zell classification numbers have been used for PBBs and PBDEs.

A.11 Alternative extraction procedures for soluble polymers

For a soluble polymer sample, especially PS-HI, the following alternative extraction procedure may be applied:

a) Weigh 100 mg of sample to the nearest 0,1 mg in an amber vial (at least 2 ml in volume).

NOTE 1 Other sample amounts may be used for samples with potentially very low or very high PBB or PBDE concentrations.

b) Transfer 9,8 ml of the appropriate solvent to the vial, and record the mass of the mixture.

NOTE 2 The solvent volume may be adjusted accordingly for samples with potentially very low or very high PBB or PBDE concentrations.

c) Add 200 µl of the DBOFB surrogate standard (A.5.1.a) (50 µg/ml) to the vial and record the new mass. Record the total mass of the sample, solvent, vial and cap.

d) Tightly cap the sample vial. Place it in an ultrasonic bath and sonicate for 30 min until the sample has been dissolved. A small piece of adhesive tape may be used to prevent the cap from vibrating loose. After the sample is dissolved, allow the vial to cool and record the mass. Verify that the mass is the same as recorded in step c) above.

e) Transfer 1,0 ml of the solution to a new amber vial (at least 12 ml in volume) and weigh the aliquot to the nearest 0,1 mg.

f) Choose a non-solvent for the polymer that is a good solvent for PBB/PBDE. Transfer 9,0 ml of the non-solvent to the vial and record the mass of vial and contents to the nearest 0,1 mg.

g) Allow the polymer to settle out or filter the mixture through a 0,45 μm PTFE membrane. Alternatively, transfer a 1,0 ml aliquot of solution to a 10 ml volumetric flask and weigh the aliquot accurately to 0,1 mg. Bring the volume up to the mark with fresh solvent, record the final mass, and mix well.

NOTE 3 For example, dissolve a sample of PS-HI in toluene (A.3.a), then dilute a 1,0 ml aliquot of the solution with 9,0 ml of isooctane.

h) If the polymer precipitation step was followed, prepare a 10 % solution of the solvent in the non-solvent and use a calibrated volumetric flask to determine the density of the mixture. Use this density in later calculations.

i) Prepare a blank extraction and dilution by the same procedure.

j) Follow the analytical procedures described in A.5.4 and Clauses A.6 and A.7. Calculate the PBB or PBDE concentration in the sample according to A.6.3.

A.12 Examples of chromatograms at suggested GC-MS conditions

Table A.7 shows PBB and PBDE congeners in the mixture used for the examples of chromatograms shown in Figures A.1 to A.3.

Table A.7 – PBB and PBDE congeners in the mixture

PBB congeners	PBDE congeners
B-2 = 3-Bromobiphenyl	BDE-1 = 2-Bromodiphenyl ether
B-10 = 2,6-Dibromobiphenyl	BDE-7 = 2,4-Dibromodiphenyl ether
B-30 = 2,4,6-Tribromobiphenyl	BDE-28 = 2,4,4'-Tribromodiphenyl ether
B-80 = 3,3',5,5'-Tetrabromobiphenyl	BDE-47 = 2,2',4,4'-Tetrabromodiphenyl ether
B-103 = 2,2',4,5',6-Pentabromobiphenyl	BDE-99 = 2,2',4,4',5-Pentabromodiphenyl ether
B-169 = 3,3',4,4',5,5'-Hexabromobiphenyl	BDE-100 = 2,2',4,4',6-Pentabromodiphenyl ether
B-194 = 2,2’,3,3’,4,4’,5,5’-OctaBB	BDE-154 = 2,2',4,4',5,6'-Hexabromodiphenyl ether
B-206 = 2,2’,3,3’,4,4’,5,5’,6-NonaBB	BDE-183 = 2,2',3,4,4',5',6-Heptabromodiphenyl ether
B-209 = Decabromobiphenyl	BDE-203 = 2,2',3,4,4',5,5',6-Octabromodiphenyl ether
	BDE-206 = 2,2',3,3',4,4',5,5',6-Nonabromodiphenyl ether
	BDE-209 = Decabromodiphenyl ether

The following chromatograms were obtained by using the GC parameters described in Clause A.7.

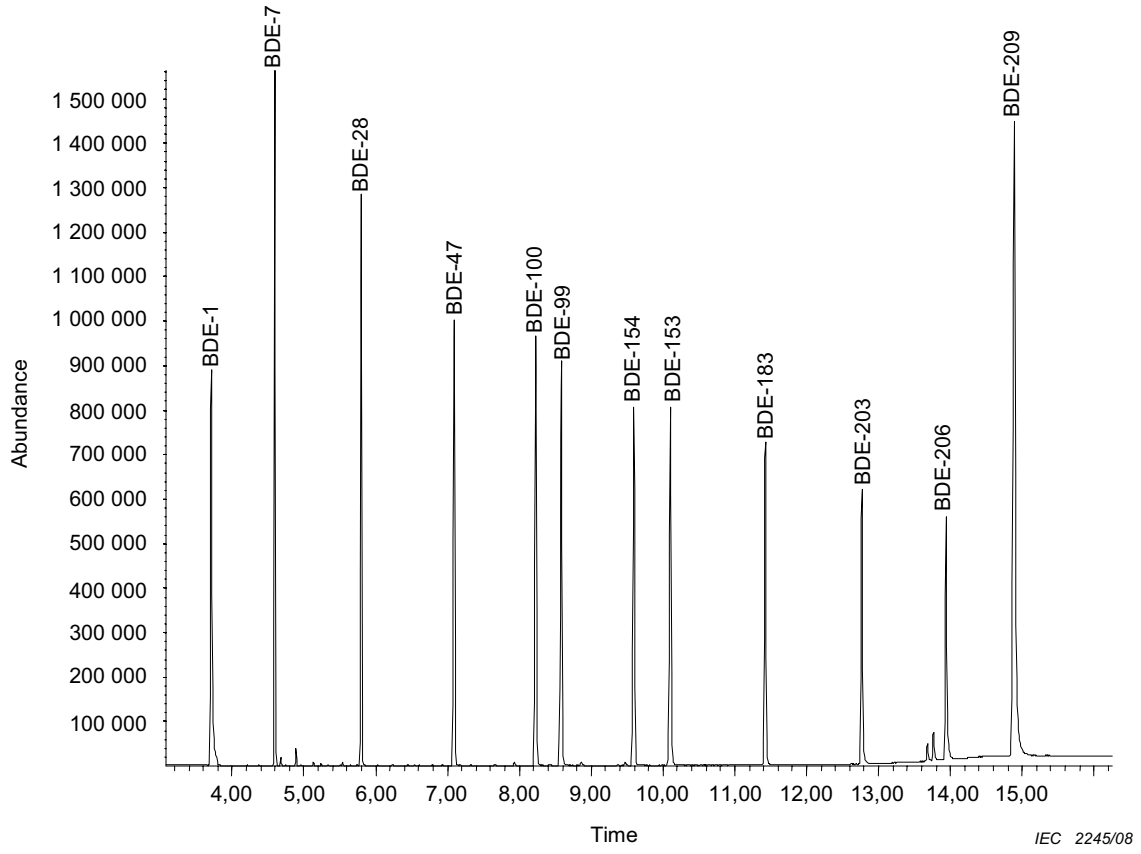

Figure A.1 – Total ion chromatogram of PBDE mixture, BDE-1 to BDE-206 (5 µg/ml), BDE-209 (50 µg/ml)

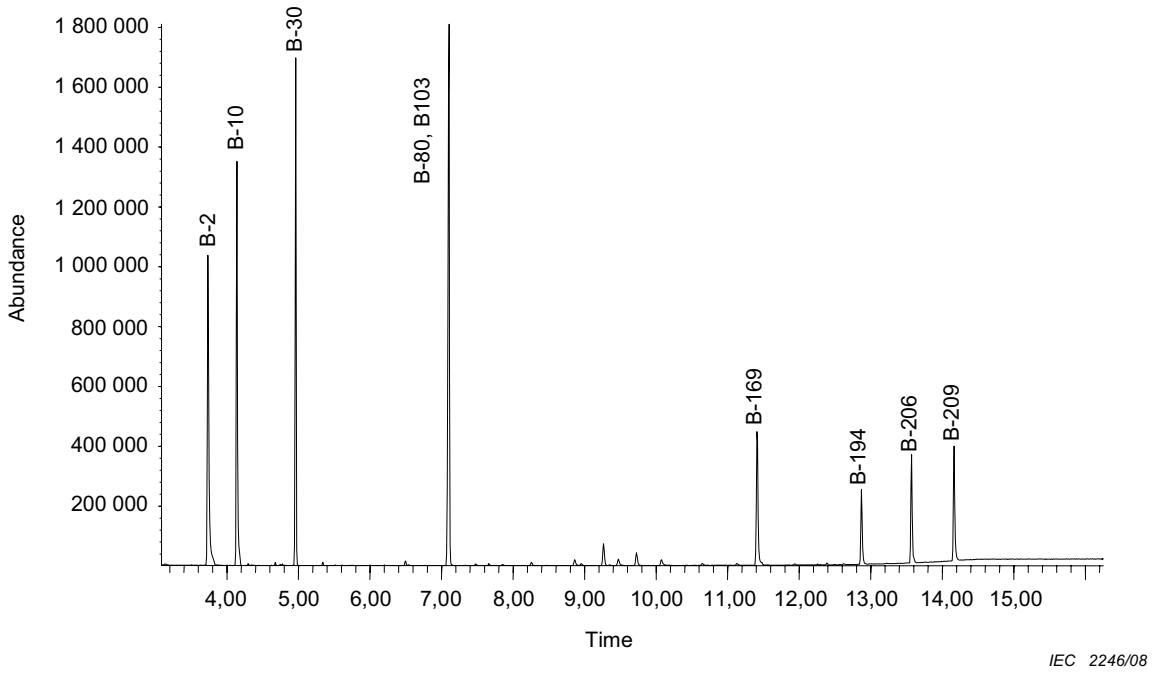

Figure A.2 – Total ion chromatogram of PBB mixture (3,5 µg/ml)

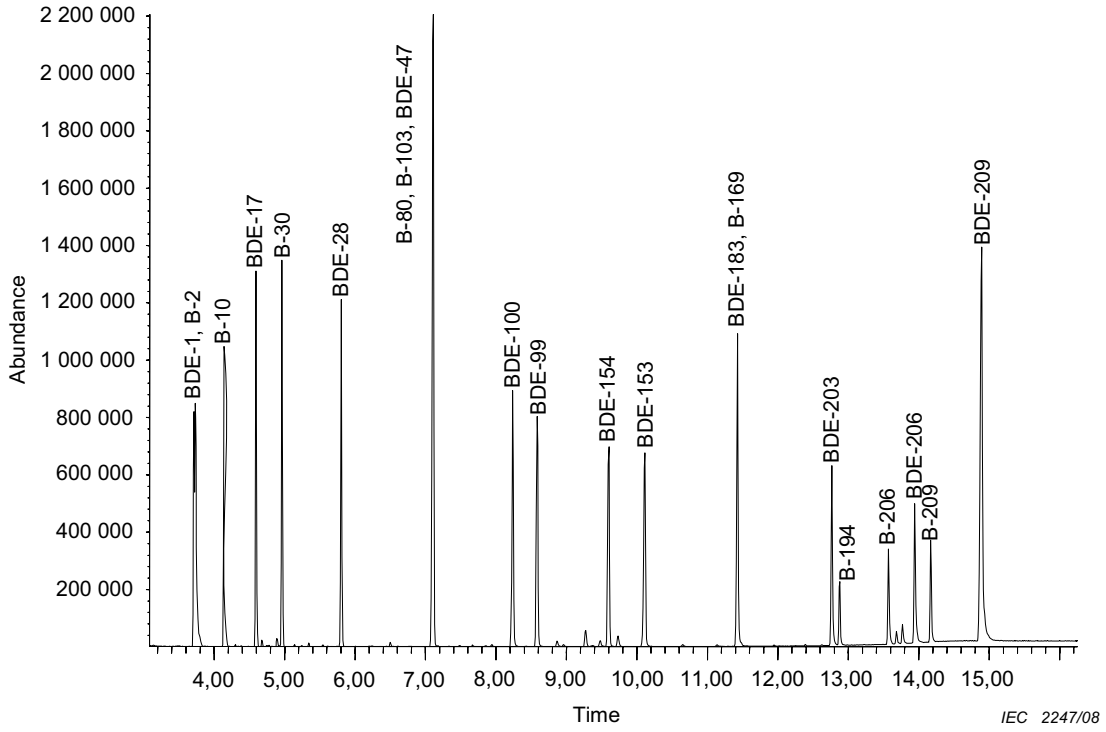

Figure A.3 – Total ion chromatogram of PBB and PBDE mixtures (BDE-1 to BDE-206 5 µg/ml, BDE-209 5,0 µg/ml, PBBs 3,5 µg/ml)

Annex B
(informative)

Test for the presence of hexavalent chromium (Cr(VI)) in colourless and coloured corrosion-protected coatings on metals

B.1 Overview

This method provides procedures for the qualitative determination of the presence of hexavalent chromium (Cr(VI)) in colourless and coloured corrosion-protection coatings on metallic samples. Cr(VI) is toxic to human beings. All potential Cr(VI)-containing samples and reagents used in the method shall be handled with appropriate precautions.

Due to its highly reactive nature, the concentration of Cr(VI) in a corrosion-protection coating layer can change drastically with time and storage conditions. Therefore this method takes a practical and effective approach to qualitatively detecting the presence of Cr(VI) in the coating layer. The samples to be tested shall be stored at ambient conditions and the analytical method described here shall be carried out within 30 days of the coating process. Ambient conditions are defined as 45 % RH to 75 % RH (relative humidity) and temperature between 15 °C and 35 °C. If a sample cannot meet the requirement of being stored at ambient conditions and analysed within 30 days of the coating process, or if a sample has an unknown storage conditions and production date, the analytical result of the sample obtained by following the method described here cannot verify whether Cr(VI) was originally present in the coating layer. The results can only give an indication of the presence/absence of Cr(VI) within the limitations of the method at the time of testing. It shall also be clearly stated in the analytical report.

This method contains two main procedures: the spot-test procedure and the boiling water extraction procedure. The spot-test procedure may be conducted first for its simplicity and ease of use. When the spot-test shows a negative result after finishing all the procedures listed in B.5.1, or an analyst is not certain about the result from a spot-test, or there is colour interference from the background, the boiling water extraction procedure shall be conducted for verification. Colour interference can often be found in coloured corrosion protection coatings and cause a false test result. When the presence of Cr(VI) in a sample is detected using the spot-test procedure or the boiling water extraction method, the sample is considered to have Cr(VI) in the coating layer.

NOTE The Cr(VI) comparison standard solutions used in this method were chosen on the basis of two international inter-laboratory studies (IIS) organized by IEC TC 111 WG3. The test results are expressed in terms of positive and negative for the presence of Cr(VI). Refer to Clause B.6 for details.

Solutions or waste material containing Cr(VI) shall be disposed of properly. For example, ascorbic acid or other reducing agent can be used to reduce Cr(VI) to Cr(III).

B.2 Apparatus, equipment and materials

The following items shall be used for the analysis:

a) Calibrated balance: analytical balance with an accuracy of 0,1 mg.

b) Thermometer or other temperature measurement device capable of measuring up to 100 °C.

c) Colorimetric instrument: either a spectrophotometer for use at 540 nm, providing a light path of 1 cm or longer; or a filter photometer, providing a light path of 1 cm or longer and equipped with a greenish-yellow filter having maximum transmittance near 540 nm.

d) Labware: all re-usable labware (glass, quartz, polyethylene, polytetrafluoroethylene (PTFE), etc.), including the sample containers, shall be soaked overnight in laboratory-

grade detergent and water (B.3.g), rinsed with water (B.3.g), and soaked for 4 h in a mixture of dilute acids (HNO_3:HCl:H_2O = 1:2:9 by volume) followed by rinsing with water (B.3.g). Alternative cleaning procedures are permitted, provided adequate cleanliness can be demonstrated through the analysis of method blanks.

e) Volumetric graduated cylinders: Class A glassware, 100 ml, or equivalent of acceptable precision and accuracy. Alternative volumetric equipment, e.g. automatic dilutors, with acceptable precision and accuracy can be used.

f) Assorted calibrated pipettes: Class A glassware or equivalent of acceptable precision and accuracy.

g) Extraction vessel: borosilicate glass or quartz beaker with volume graduation of 250 ml, or equivalent.

h) Heating device: capable of maintaining boiling of the extraction solution.

i) Filter membranes (0,45 μm), preferably cellulose-based or polycarbonate membranes.

B.3 Reagents

The following reagents shall be used:

a) 1,5-diphenylcarbazide, analytical reagent grade.

b) Potassium dichromate $K_2Cr_2O_7$ standard solution (containing 400 mg/kg total Cr): In a glass container, dissolve 0,113 g of $K_2Cr_2O_7$ (analytical reagent grade) in water (B.3.g) and dilute with water (B.3.g) to a total mass of 100 g. Cap or stopper the container tightly. The shelf life of this solution is about one year.

c) $K_2Cr_2O_7$ standard solution (containing 1 mg/kg total Cr): Into a glass container, measure 0,25 g of the solution from step b) and dilute with water (B.3.g) to a total mass of 100 g. Cap or stopper the container tightly. This solution shall be used within 24 h after preparation.

d) Acetone, analytical reagent grade.

e) Ethanol C_2H_5OH (96 % (v/v)), analytical reagent grade.

f) Orthophosphoric acid H_3PO_4 solution (75 % (m/m)), analytical reagent grade.

g) Water: Grade 1 specified in ISO 3696, which shall be free of interferences.

B.4 Sample preparation

Prior to the test, the sample surface shall be free of all contaminants, fingerprints and stains. If the surface is coated with thin oil, it shall be removed prior to the test by using a clean, soft laboratory wipe wetted with a suitable solvent, or by rinsing the surface with a suitable solvent at room temperature (not exceeding 35 °C). The samples shall not be subject to forced drying at temperature in excess of 35 °C. Treatment in alkaline solutions shall not be performed as corrosion-protection coatings are broken down by alkalis.

If there is a polymer coating on a sample surface, gentle abrasion with a fine sandpaper, such as a SiC grinding paper with 800 grit size, may be performed to remove the polymer layer, but without removing the corrosion protection coating on the sample. Other coating removal methods may be applied if they are proven to be of equal or greater effectiveness.

B.5 Test procedures

B.5.1 Spot-test procedure

For the spot-test procedure the following steps are carried out:

a) Dissolve 0,4 g of 1,5-diphenylcarbazide (B.3.a) in a mixture of 20 ml acetone (B.3.d) and 20 ml ethanol (96 % (v/v), B.3.e). After dissolving, add 20 ml of 75 % (m/m)

orthophosphoric acid solution (B.3.f) and 20 ml of water (B.3.g). Prepare this solution no more than 8 h prior to use.

b) For a metal plate sample, place 1 to 5 drops of test solution (prepared in B.5.1.a) on the sample surface. If Cr(VI) is present, a red to violet colour will appear within a few minutes. The test result is considered as positive. Otherwise, the test result is considered as negative. The colour change or a positive test result can be confirmed by following the procedures described in B.5.1.d) 4th and 5th bullets. Ignore any colour that appears much later, for example on drying

For a fastener sample, e.g. a small screw, place the sample in a small container, such as a test tube, and add 1 to 5 drops of test solution (prepared in B.5.1.a) to the container. If Cr(VI) is present, a red to violet colour will appear within a few minutes. It is easier to observe the colour of test solution by removing the fastener sample from the container and putting the container against a white background.

c) If the test result is positive, the sample is considered to contain Cr(VI) in the coating layer. No further analysis is required.

d) If the test result is negative, the following steps shall be carried out:

- Choose an untested area on the sample surface of the metal plate, or choose another fastener sample of the same kind. Apply a gentle rub with an abrasive paper, such as a SiC grinding paper with 800 grit size, to scratch the possibly reduced chromate surface, but without completely removing the whole coating layer.
- On the newly scratched surface, repeat B.5.b. If the test result is positive, the sample is considered to contain Cr(VI) in the coating layer.
- If the test result is negative again, repeat the first step of B.5.d with more force to scratch deeper into the coating layer, and repeat the second step of B.5.d. If the test result remains negative upon reaching the substrate, the sample is considered below the limit of detection of Cr(VI) at the time of testing.
- If the colour developed during the test is difficult for the analyst to judge, place one drop of $K_2Cr_2O_7$ standard solution (containing 1 mg/kg Cr, prepared in B.3.c) on a newly polished bare substrate, and mix it with one drop of test solution (prepared in procedure B.5.1.a). As an alternative, mix equal amounts of $K_2Cr_2O_7$ standard solution (1 mg/kg Cr, prepared in B.3.c) and test solution (prepared in procedure B.5.1.a) in a small container, such as a test tube.
- Compare the colour obtained from the sample with the colour obtained from the $K_2Cr_2O_7$ standard solution. If the colour obtained from sample is the same or redder than the colour from the standard solution, the spot-test result for the sample is positive. If the colour obtained from the sample is clear (no colour), the test result is negative. If the colour obtained from the sample is less red than the colour from the standard solution but not clear, go to B.5.2.
- A positive spot-test result indicates the presence of Cr(VI) in the coating. The Cr(VI) concentration detected in the spot-test solution is equal to or greater than 1 mg/kg. However, it shall not be interpreted as the Cr(VI) concentration in the coating layer of the sample and shall not be used as a method detection limit for this qualitative test.

e) For comparison purposes, test the substrate of the sample similarly. The substrate of the sample can be reached by removing all the coating layers on the sample surface, for example, abrasion with abrasive paper or a file, or by stripping the coating layer with acid solutions.

f) When the spot-test shows a negative result, or the analyst is not certain about the spot-test result obtained, the boiling water extraction procedure in B.5.2 shall be used to verify the result.

B.5.2 Boiling water extraction procedure

a) The test solution prepared in B.5.1.a can be used directly in this procedure. An alternative test solution with a much longer shelf life can also be used in this procedure. Prepare the alternative solution as follows. dissolve 0,5 g of diphenylcarbazide (B.3.a) in 50 ml of acetone (B.3.d). Dilute slowly, while stirring, with 50 ml of water (B.3.g) (rapid mixing may result in precipitation of diphenylcarbazide). For maximum stability, store this test solution

under refrigeration in an amber glass bottle. Discard when the solution becomes discoloured.

b) The sample to be tested shall have a surface area of 50 $cm^2 \pm 5$ cm^2. For small parts, such as fasteners or samples with irregular surface shapes, use a suitable number of samples to obtain the total required surface area of 50 $cm^2 \pm 5$ cm^2.

NOTE 1 For a sample with a complex shape, its surface area can be estimated according to its manufacturing specifications if available, or by using its dimensions and shape. For example: a flat-headed countersunk screw may be considered as one metal cylinder (the screw body) adjacent to one metal cone (the screw head).

Estimated surface area of the screw body:

$$S_b = 2\pi R_b H_b + 2\pi (R_b)^2 \quad \text{(B.1)}$$

where

S_b is the estimated surface area of the screw body;

R_b is the radius of the screw body;

H_b is the height of the screw body.

Estimated surface area of the screw head:

$$S_h = \pi(R_c + R_b)H_h + \pi R_c^2 \quad \text{(B.2)}$$

where

S_h is the estimated surface area of the screw body;

R_c is the top radius of the screw head;

H_h is the height of the screw head.

Total estimated surface area of the screw:

$$S_t = S_h + S_b - 2\,\pi(R_b)^2 \quad \text{(B.3)}$$

where

S_t is the total estimated surface area of the screw.

NOTE 2 It may be difficult to obtain a total surface area of 50 $cm^2 \pm 5$ cm^2 for some small electronic parts. In that case, a reduced total sample surface may be used, and the dilution factor is adjusted accordingly. The adjustment should be recorded on the analysis report.

c) Heat 50 ml of water (B.3.g) in a suitable beaker (with volume graduation) (B.2.d) to boiling, and totally immerse the sample(s) inside the beaker (B.2.d). Cover the beaker (B.2.d) with a watch glass (B.3.d). Leach for 10 min ± 0,5 min while the water continues to boil. Remove the sample(s), and cool the beaker (B.2.d) and its contents to room temperature. If some water evaporates, fill with water (B.3.g) back to 50 ml. If the solution is milky or has a precipitate, filter it through a membrane filter (B.2.i) into a dry beaker (B.2 d). Add 1 ml of orthophosphoric acid solution (8.3.f) and mix well. Pour half (approximately 25 ml) the solution into another dry beaker (B.2.d). Add 1 ml test solution (B.5.1.a or B.5.2.a) to one of the two beakers (B.2.d), mix and observe the colour against the solution in the other beaker (B.2.d), which serves as the blank. A red colour indicates the presence of Cr(VI).

d) If the colour developed during the test is difficult for the analyst to judge, transfer a portion of the solution to a 1 cm absorption cell (B.2.c). After a reaction time of 2 min, measure the absorbance at 540 nm against the blank with the colorimetric instrument (B.2.c). Make three measurements and take the average as the final absorbance of the sample.

e) Dilute 1 ml of $K_2Cr_2O_7$ standard solution (containing 1 mg/kg Cr, prepared in B.3.c) to 50 ml with water (B.3.g). Add 1 ml of orthophosphoric acid solution (B.3.f) and mix well. Add 2 ml test solution (B.5.1.a or B.5.2.a), mix and measure the absorbance three times as above. Take the average of three measurements as the final absorbance of the standard solution.

f) If the absorbance value obtained in B.5.2.d is equal to or greater than that obtained in B.5.2.e, the sample is considered to be positive for Cr(VI). If not, the test result is negative.

g) A positive boiling water extraction test result indicates the presence of Cr(VI). The Cr(VI) concentration detected in the boiling water extraction solution is equal to or greater than 0,02 mg/kg with a sample surface area of 50 cm^2 used. However, it shall not be interpreted as the Cr(VI) concentration in the coating layer of the sample and shall not be used as a method detection limit for this qualitative test.

B.6 Evaluation of the method

The principle of this method was evaluated and supported by two international inter-laboratory studies (IIS) organized by IEC TC 111 WG3. The studies were focused on detecting the presence of Cr(VI) in the corrosion protection coatings on metallic samples. Fourteen international laboratories participated in the first study and twelve in the second study.

The Cr(VI) comparison standard solutions in this method, namely 0,5 mg/kg for spot-test procedures and 0,02 mg/kg for boiling water extraction procedures, were decided on the results from two IIS. Different comparison standard solutions can also be found in other Cr(VI)-related standard method(s), e.g. EN 15205:2006[49] where a 0,1 µg/cm^2 threshold is utilized as a qualitative comparison, above which a sample is found to contain Cr(VI). This threshold has not been evaluated under the scope of this method. Also note that different units are used in the different methods.

Annex C
(Informative)

Determination of hexavalent chromium (Cr(VI)) in polymers and electronics by the colorimetric method

C.1 Overview

This method describes procedures to measure hexavalent chromium, Cr(VI), quantitatively in samples of polymers and electronic components. This method uses alkaline digestion procedures to extract Cr(VI) from samples. Studies have shown that alkaline solution is more effective than acidic solution in extracting Cr(VI) from water-soluble and water-insoluble samples. Minimal reduction of native Cr(VI) to Cr(III) or oxidation of native Cr(III) to Cr(VI) occurs in the alkaline extraction solution.

The alkaline extraction solution is a mixture of 0,28 mol/l Na_2CO_3 and 0,5 mol/l NaOH. A target sample is digested in the solution at 90 °C to 95 °C for 3 h. The Cr(VI) concentration in the extract is determined by its reaction under acidic conditions with 1,5-diphenylcarbazide. Cr(VI) is reduced to Cr(III) in the reaction with diphenylcarbazide which is oxidized to diphenylcarbazone. The Cr(III) and diphenylcarbazone further form a red-violet-coloured complex in the reaction. The complex solution is measured quantitatively by a colorimeter or a spectrophotometer at 540 nm.

To retard the chemical activity of Cr(VI), the samples and extracts shall be stored until analysis at ambient conditions of 45 % to 75 % relative humidity and 15 °C to 35 °C. Since the stability of Cr(VI) in extracts is not completely understood, the analyses shall be carried out as soon as possible after extraction.

An international inter-laboratory study organized during the development of this method found that Cr(VI) extraction is heavily affected by the sample matrix. The suitability of this method is therefore variable and dependent on the specific compositional matrix of the sample under test. Every sample shall be evaluated by the matrix spike procedure described in C.4.5.2 to determine whether the method is applicable to the target sample and whether the analysis result must be adjusted according to the matrix spike recovery rate. Inter-laboratory study results suggest that this method is suitable for certain polymer sample types, including polyvinyl chloride (PVC) and acrylonitrile butadiene styrene (ABS), but is not suitable for an ethylene vinyl acetate/polyethylene copolymer (EVAC/PE).

One practical approach to measure the total Cr, including Cr(VI), quantitatively in samples of polymers and electronic components is to use inductively coupled plasma methods (ICP) similar to the methods described in Clauses 8 to 10. However, ICP cannot selectively detect Cr(VI); it determines the amount of total Cr in all chemical forms in the samples.

Possible interferences may be caused by reduction of Cr(VI), oxidation of Cr(III), or colour interference in the colorimetric measurement. The interference parameters may include, but are not limited to, pH, Fe^{2+}, S^{2-}, Mo(VI) and Hg salts.

All potential Cr(VI)-containing samples and reagents used in the method shall be handled with appropriate precautions. Solutions or waste material containing Cr(VI) shall be disposed of properly. For example, ascorbic acid or some other reducing agent can be used to reduce Cr(VI) to Cr(III).

C.2 Apparatus, equipment and materials

C.2.1 Apparatus

a) Vacuum filtration apparatus.

b) Heating and stirring device capable of maintaining the digestion solution at temperatures between 90 °C and 95 °C with continuous stirring capability. A polytetrafluoroethylene (PTFE)-coated magnetic stirring rod can be used for polymer samples. However, it is not recommended for ferromagnetic samples, such as those commonly found in metallic and electronic samples. In that case, an overhead stirrer with a PTFE shaft and paddle is recommended.

c) Calibrated pH meter to read pH range 0 to 14 with an accuracy ± 0,03 pH units.

d) Analytical balance capable of measurement to 0,1 mg.

e) Thermometer, thermistor or other temperature measurement device capable of measuring up to 100 °C.

f) Colorimetric instrument: either a spectrophotometer for use at 540 nm, providing a light path of 1 cm or longer; or a filter photometer, providing a light path of 1 cm or longer and equipped with a greenish-yellow filter having maximum transmittance near 540 nm.

g) Grinding mill, with or without LN_2 cooling, capable of grinding polymer samples and electronic components.

C.2.2 Equipment

a) Labware: all re-usable labware (glass, quartz, polyethylene, PTFE, etc.), including the sample containers, shall be soaked overnight in laboratory-grade detergent and water (C.3.n), rinsed with water (C.3.n), and soaked for 4 h in a mixture of dilute HNO_3 and HCl (HNO_3:HCl:H_2O = 1:2:9 by volume) followed by rinsing with water (C.3.n). Alternative cleaning procedures are permitted, provided that adequate cleanliness can be demonstrated through the analysis of method blanks.

b) Volumetric flasks and graduated cylinders: Class A glassware, 1 000 ml and 100 ml, with stoppers, or equivalent of acceptable precision and accuracy. Alternative volumetric equipment, e.g. automatic dilutors, with acceptable precision and accuracy can be used.

c) Assorted calibrated pipettes of acceptable precision and accuracy.

d) Digestion vessel: a suitable borosilicate glass or quartz beaker with volume graduation of 250 ml or equivalent.

e) Filter membranes (0,45 µm): preferably cellulose-based or PC membranes.

f) C18 syringe filter cartridge.

C.3 Reagents

a) Nitric acid: ρ(HNO_3) = 1,40 g/ml, 65 % (m/m), analytical reagent grade or spectroscopic grade. Store at 20 °C to 25 °C in the dark. Do not use concentrated HNO_3 if it has a yellow colour, which is indicative of photoreduction of NO_3^- to NO_2, a reducing agent for Cr(VI).

b) Sodium carbonate: Na_2CO_3, anhydrous, analytical reagent grade. Store at 20 °C to 25 °C in a tightly sealed container.

c) Sodium hydroxide: NaOH, analytical reagent grade. Store at 20 °C to 25 °C in a tightly sealed container.

d) Magnesium chloride: $MgCl_2$ (anhydrous), analytical reagent grade. A mass of 400 mg $MgCl_2$ is approximately equivalent to 100 mg Mg^{2+}. Store at 20 °C to 25 °C in a tightly sealed container.

e) Phosphate buffer: To prepare a buffer solution at pH 7, dissolve 87,09 g K_2HPO_4 (analytical reagent grade) and 68,04 g KH_2PO_4 (analytical reagent grade) into 700 ml of water (C.3.n). Transfer to a 1 l volumetric flask (C.2.2.a) and dilute to volume. As prepared, the solution will contain 0,5 mol/l K_2HPO_4 and 0,5 mol/l KH_2PO_4.

f) Lead chromate: $PbCrO_4$, analytical reagent grade. Store at 20 °C to 25 °C in a tightly sealed container. This is the solid matrix spike agent.

g) Digestion solution: Dissolve 20,0 g ± 0,05 g NaOH and 30,0 g ± 0,05 g Na_2CO_3 in water (C.3.n) in a 1 l volumetric flask (C.2.2.a) and dilute to the mark. Store the solution in a tightly capped polyethylene bottle at 20 °C to 25 °C, and prepare fresh monthly. The pH of the digestion solution shall be checked before using. If the pH is <11,5, discard the solution and prepare a fresh batch.

h) Potassium dichromate stock solution: Dissolve 141,4 mg of dry $K_2Cr_2O_7$ (analytical reagent grade) in water (C.3.n) and dilute to 1 l in a volumetric flask (C.2.2.a) (1 ml contains 50 µg Cr).

i) Potassium dichromate standard solution: Dilute 10 ml potassium dichromate stock solution (C.3.h) with water (C.3.n) to 100 ml in a volumetric flask (C.2.2.a) (1 ml contains 5 µg Cr).

j) Sulfuric acid, 10 % (v/v): Dilute 10 ml of distilled reagent grade or spectroscopic grade H_2SO_4 to 100 ml with water (C.3.n) in a volumetric flask (C.2.2.a).

k) Diphenylcarbazide solution: Dissolve 250 mg 1,5-diphenylcarbazide in 50 ml acetone (C.3.o). Store in a brown bottle. Prior to use, check the solution for discoloration. If the solution becomes discoloured, discard it and prepare a fresh batch.

l) Potassium dichromate, $K_2Cr_2O_7$, spike solution (1 000 mg/l Cr(VI)): Dissolve 2,829 g of dried (105 °C) $K_2Cr_2O_7$ in water (C.3.n) in a 1 l volumetric flask (C.2.2.a), and dilute to the mark. Alternatively, a 1 000 mg/l Cr(VI)-certified standard solution can be used. Store for use up to six months at 20 °C to 25 °C in a tightly sealed container.

m) Potassium dichromate, $K_2Cr_2O_7$, matrix spike solution (100 mg/l Cr(VI)): Add 10,0 ml of the 1 000 mg)/l Cr(VI) solution made from $K_2Cr_2O_7$ spike solution (C.3.l) to a 100 ml volumetric flask (C.2.2.a) and dilute to volume with water (C.3 n). Mix well.

n) Water: Grade 1 specified in ISO 3696, which shall be free of interferences.

o) Acetone, analytical reagent grade.

C.4 Sample preparation

Samples shall be collected and stored using devices and containers that do not contain stainless steel.

Prior to digestion, polymer samples and electronic components shall be ground into a fine powder (C.2.1.g) with 100 % of the material passing through a 250 µm sieve, e.g. a #60 ASTM standard sieve.

C.5 Test procedure

C.5.1 Extraction

a) Accurately weigh a sample of 2,5 g. Place the sample into a clean digestion vessel (C.2.2.d).

NOTE 1 Alternative sample amounts may be used for samples with potentially very low or very high Cr(VI) concentrations.

b) To test for recovery in every matrix, accurately weigh a second sample of 2,5 g (or another chosen amount of sample), and place it into a second, clean digestion vessel (C.2.2.d). Choose a spike solution (C.3.l) or C.3.m) and add it directly to the sample.

c) To each sample add 50 ml of digestion solution (C.3.g) measured with a graduated cylinder (C.2.2.a).

d) Next, add 400 mg $MgCl_2$ dissolved in 0,5 ml of 1,0 mol/l phosphate buffer (C.3.e) to each sample. It is optional to add $MgCl_2$ to the solution if the analytical techniques used can correct for the possible method-induced oxidation/reduction of chromium.

NOTE 2 For polymer samples that appear to “float” on the surface of the digestion solution, 1 or 2 drops of a wetting agent (e.g. “Triton X”) may be added at this time to increase the sample wetting during digestion. Cover all digestion vessels with watch glasses or plastic covers.

e) Heat the samples to 90 °C to 95 °C with continuous stirring (C.2.1.b). Then maintain the samples at 90 °C to 95 °C for at least 3 h with constant stirring. After 3 h, cool to room temperature with continued stirring.

f) Filter through a 0,45 µm membrane filter (C.2.2.e). Rinse the digestion vessel (C.2.2.d) three times with water (C.3.n) with the rinse solution added to the filter (C.2.2.e). If the filter becomes clogged using the 0,45 µm membrane filter, a large pore size filter paper may be used to pre-filter the samples.

g) Rinse the inside of the filter flask and the filter pad (C.2.2.e) with water (C.3.n) and transfer the filtrate and the rinse solutions to a clean 250 ml vessel (C.2.2.a). Save the solids collected on the filter (C.2.2.e) for possible use in assessing low Cr(VI) matrix spike recoveries. Store the filtered solids at 4 °C ± 2 °C.

h) With constant stirring while monitoring the pH, add HNO3 (C.3.a) drop-wise to the 250 ml vessel (C.2.2.a). Adjust the pH of the solution to 7,5 ± 0,5. Remove the stirring device (C.2.1.b) and rinse, collecting the rinse solution in the beaker (C.2.2.a). Transfer the contents of the vessel quantitatively to a 100 ml volumetric flask (C.2.2 a) and fill to the mark with water (C.3.n). Mix well. The digestate is ready for analysis.

C.5.2 Colour development and measurement

a) Transfer 95 ml of the digestate to be tested to a clean 100 ml vessel (C.2.2.a). Slowly add H_2SO_4 solution (C.3.j) to the vessel and adjust the pH of the solution to 2,0 ± 0,5. If the solution is clear proceed to C.5.2.d. If the solution is turbid, contains a flocculent precipitate (cloudy, flake-like and non-crystalline), or colour is present, proceed to C.5.2.b.

b) If the solution is turbid or flocculent precipitates are present, filter the sample through a 0,45 µm membrane filter (C.2.2.e) or slow-rate filter paper. If colour is present in the sample solution, filter the solution with a C18 syringe cartridge (C.2.2.f) before adding diphenylcarbazide solution (C.3.k). If the digestate is clear after either filtration step, proceed to C.5.2.d. If the digestate is coloured or turbid after either filtration step, proceed to C.5.2.c.

c) Transfer each of the turbid digestates quantitatively to a 100 ml volumetric flask (C.2.2.a) and bring to volume with water (C.3.n). Invert several times to mix. Remove approximately 5 ml from the flask and record an absorbance reading after zeroing the UV instrument (C.2.1.f) with the 0,0 µg/ml standard. Add 2,0 ml diphenylcarbazide solution (C.3.k) to each of the turbid digestion solutions, mix and adjust the sample volumes to 100 ml with water (C.3.n). Invert several times to mix and let stand 5 min to 10 min for full colour development. Proceed to C.5.2.d).

d) Transfer the contents of the vessel quantitatively to a 100 ml volumetric flask (C.2.2.a), add 2,0 ml diphenylcarbazide solution (C.3.k) and adjust the sample volume to 100 ml with water (C.3.n). Invert several times to mix and let stand 5 min to 10 min for full colour development.

e) Transfer an appropriate portion of the solution to a 1 cm absorption cell and measure its absorbance at 540 nm with a colorimetric instrument (C.2.1.f).

f) Correct the absorbance reading of the sample by subtracting the absorbance of a blank carried through the colour development procedures. For the filtered solutions in C.5.2.b), correct the absorbance by subtracting the absorbance reading from step C.5.2.c).

g) From the corrected absorbance, determine the concentration of Cr(VI) present by referring to the calibration curve.

C.5.3 Preparation of the calibration curve

a) Pipette the Cr(VI) standard solution (C.3.i) in measured volumes into 10 ml volumetric flasks (C.2.2.a) to create concentrations ranging from 0,1 mg/l to 5,0 mg/l Cr(VI) when diluted to volume. Prepare a blank and a minimum of three standard solutions.

NOTE An alternative concentration range of the standard solutions may be used if the Cr(VI) concentration in the sample solution is outside the original calibration curve. The sample solutions may also be diluted if they are more concentrated than the highest calibrant solution.

b) Develop the colour of the standard solutions as for the samples using the procedure in C.5.2.

c) Transfer an appropriate portion of the solution to a 1 cm absorption cell and measure the absorbance at 540 nm using the colorimetric instrument (C.2.1.f).

d) Correct the absorbance reading by subtracting the absorbance of a blank carried through the colour development procedure.

e) Construct a calibration curve by plotting corrected absorbance values versus concentration of Cr(VI). Either linear regression or quadratic fitting can be applied to establish a calibration curve. The correlation coefficient (R^2) of the curve shall be >0,99, or a new calibration curve shall be created.

C.5.4 Calculation of analytical results

a) Cr(VI) concentration (μg/g) in total sample:

$$C = \frac{A \times D \times F}{S} \tag{C.1}$$

where

C is the Cr(VI) concentration in μg/g;

A is the concentration observed in the digestate in μg/ml;

D is the dilution factor;

F is the final volume of the digestate in ml;

S is the initial sample mass in g.

b) Relative per cent difference:

$$R = \frac{|S - D|}{0{,}5 \times (S + D)} \times 100 \tag{C.2}$$

where

R is the relative per cent difference in %;

S is the Cr(VI) concentration in sample observed in the initial test in μg/g;

D is the Cr(VI) concentration in sample observed in the duplicated test in μg/g.

NOTE 1 A similar calculation listed in (C.4.4.a) can also be used to obtain the Cr(VI) concentrations in the initial and duplicated tests.

c) Spike recovery:

$$SR = \frac{SS - US}{SA} \times 100 \tag{C.3}$$

where

SR is the spike per cent recovery in %;

SS is the Cr(VI) concentration in the spiked sample in μg/g;

US is the Cr(VI) concentration in the unspiked sample in μg/g;

SA is the Cr(VI) concentration used in the spike solution in μg/g.

NOTE 2 A similar calculation listed in (C.5.4.a) can also be used to obtain the Cr(VI) concentrations in the spiked sample, unspiked sample.

C.5.5 Quality control

C.5.5.1 General method

Samples shall be analysed in batches of not more than 20 samples counting all samples, any blanks, any duplicates and any spike recovery tests. A minimum of one blank per batch shall be prepared and analysed to test for contamination and memory effects. In every batch, at least one sample shall be prepared in duplicate. Results for duplicate samples shall have a relative difference of ≤ 20 % or the batch shall be reanalysed. A laboratory control sample shall be analysed at a frequency of one per batch. The control sample shall be either of the following:

a) utilize the matrix spike solution (C.3.m) to spike 50 ml of digestion solution (prepared in C.3.h) from one sample material; or

b) utilize the solid matrix spike agent $PbCrO_4$ (C.3.f) to spike into 50 ml of digestion solution (prepared in C.3.h). Acceptable recovery shall be in the range of 80 % to 120 % or the sample batch shall be re-analysed.

C.5.5.2 Matrix spike recovery correction method

Because this test method is subject to relatively strong matrix effects, it is necessary to demonstrate the matrix spike recovery for every sample having a unique origin. Unique origin includes any of the following circumstances: different customer (even if same polymer as prior sample); different production batch (even if same polymer as prior sample); different polymer; different additives (even if same polymer as prior sample); and all other cases of changes in sample origin. The matrix spike recovery test begins with spiking the sample prior to digestion, carrying the spike through the digestion and colour development.

a) A pre-digestion matrix spike sample shall be analysed for each unique sample. Choose one of the following two options:
   - Spike the sample with 1,0 ml of the matrix spiking solution (C.3.m) or at twice the sample concentration, whichever is the greater.
   - Spike the sample by accurately weighing a minimum of 1,0 mg of $PbCrO_4$ (C.3.f) or enough $PbCrO_4$ to double the sample concentration, whichever is the greater.

b) Carry the spiked sample through the digestion and colorimetric measurement procedures beginning with C.4.1.

c) An acceptance range for matrix spike recovery shall be 10 % to 125 %, or the sample shall be re-analysed. In the case of <10 % recovery, double the matrix spiking solution amount in the re-analysis. In the case of >125 % recovery, repeat the analysis with the same amount of spiking solution in the re-analysis. If the recovery from the repeat analysis is still outside the range of 10 % to 125 %, the method is considered not applicable to the sample analysed, and the result cannot be reported.

d) If recovery is >75 % or <125 %, the result for the sample and the LOD shall not be corrected.

e) If recovery for a sample is between 10 % and 75 %, both the result and limit of detection (LOD) (see Clause C.6) for the sample shall be corrected according to the recovery. That is, multiply the result by the ratio (100 %/spike recovery). Then multiply the estimated LOD for the method by the same ratio.

f) If the sample test result corrected as in C.5.5.2.e) is greater than the estimated LOD corrected as in C.5.5.2.e), report the corrected test result. Otherwise report the corrected LOD value as the result for that sample.

EXAMPLE Assuming an estimated LOD of 2 μg/g Cr(VI) of sample and a 50 % matrix spike recovery for a sample, the corrected LOD for that test sample = 2 μg/g × (100 %/50 %) = 4 μg/g. If the test result is 100 μg/g, the corrected test result = 100 μg/g × (100 %/50 %) = 200 μg/g. In this case, the reported result is 200 μg/g.

C.6 Determination of method detection limit and limit of quantification

Clause 4 provides a general description of method detection limits and limits of quantification. The following experimental procedure is performed to determine the method detection limit and limit of quantification for Cr(VI) in polymers and electronics.

a) Accurately weigh 2,5 g of a milled (see Clause C.4) polymer or electronic sample known not to contain Cr(VI) (e.g. IRMM VDA reference material) or other compounds that may interfere with the analysis and place it in a 250 ml beaker (C.2.2.a). Repeat this step a minimum of 5 times.

b) Spike each of the beakers (C.2.2.a) with 10 µg Cr(VI) using 100 µl of the matrix spiking solution (see C.3.m).

c) Follow the test procedure in C.5.1 (excluding (C.5.1 b), C.5.2 and C.5.3).

d) Calculate the Cr(VI) concentration (µg/g) as indicated in (C.5.4.a) and determine the percent recovery of the spiked Cr(VI) for each of the samples.

$$SR = \frac{C \times M}{SA} \times 100 \qquad \text{(C.4)}$$

where

SR is the rate of recovery in % of the spiked Cr(VI);

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 Cr(VI) 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 C.1.

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 C.1 – 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.

C.7 Evaluation of the method

An international inter-laboratory study (IIS) organized by WG3 of IEC TC 111 during the development of this method found that Cr(VI) extraction is strongly affected by the sample matrix. The suitability of this method is therefore variable and dependent on the specific compositional matrix of the sample under test. Study results demonstrated a wide range of results for three polymer types containing levels of Cr(VI) between 250 µg/g and 1 100 µg/g. Results for a PVC material exhibited reproducibility up to 3,9 % relative standard deviation and Cr(VI) recovery of approximately 70 % among six laboratories. For an ABS material available as a certified reference material, the reproducibility was approximately 13 % relative standard deviation and Cr(VI) recovery was approximately 27 %. Results for an EVAC/PE material exhibited no measurable recovery.

Annex D
(informative)

Practical application of screening by X-ray fluorescence spectrometry (XRF)

D.1 Introductory remark

This annex provides general information to aid in the practical application of the method described above. Some manufacturers may provide a Standard Operating Procedure (SOP) with the instrument. Following the recommendation contained in such a document assures the operator of the best possible quality of analytical results.

D.2 Matrix and interference effects

As a general guide, the user of this method is advised that limitations in corrections for spectral interference and matrix variations from material to material may significantly affect the sensitivity, detection limit or accuracy of each analyte. The following list covers the most common issues:

a) The intensity of characteristic radiation of the element in the sample is adversely influenced by the process of scattering of the excitation radiation, which contributes to the spectral background. In addition, two major effects occur:
   1) Absorption of excitation radiation and fluorescence radiation by the analyte and by the other elements (matrix) in the sample.
   2) Secondary excitation (enhancement) of the analyte by other elements in the sample:
      – Polymers: In polymer samples the matrix influence on the analyte characteristic X-ray intensity comes from:
        - the scattering (mainly incoherent) of the primary radiation, which contributes heavily to the spectral background.
        - the absorption of the fluorescence radiation mainly by Cl in PVC, by additive elements such as Ca, Ti, Zn, Sn, and by such elements as Br and Sb, which originate in flame retardants.
        - the secondary excitation by elements such as Sb, Sn, and Br.
        - some high-powered WDXRF (>500 W) spectrometers can alter the surface of a polymer sample if exposed to the tube for long periods of time. A newly prepared sample shall always be used in this case.
      – Metals: In metal samples the scattering of the primary radiation, while still present, does not play an important role. The matrix effect is mainly caused by absorption and secondary excitation effects. These will be different for each metal matrix. The following list shows some typical elements in the various matrices:
        - Fe alloys: Fe, Cr, Ni, Nb, Mo, W,
        - Al alloys: Al, Mg, Si, Cu, Zn,
        - Cu alloys: Cu, Zn, Sn, Pb, Mn, Ni, Co,
        - Solder alloys: Pb, Cu, Zn, Sn, Sb, Bi, Ag,
        - Zn alloys: Zn, Al,
        - Precious metals alloys: Rh, Pd, Ag, Ir, Pt, Au, Cu, Zn,
        - Other metals such as Ti, Mg.
      – Electronics: In principle all effects that are described for polymers and metals.

b) In addition, the intensity of characteristic radiation of the element in the sample can be influenced by interfering lines from other elements in the sample. For the target elements these can typically be the following:

- Cd: Interferences possible from Br, Pb, Sn, Ag and Sb;
- Pb: Interferences possible from Br, As, Bi;
- Hg: Interferences possible from Br, Pb, Bi, Au and from Ca and Fe if the samples contain Ca and Fe in high concentrations;
- Cr: Interferences possible from Cl;
- Br: Interferences possible from Fe, Pb and Hg. On rare occasions an interference from Al might be experienced if BrL_{α} line is selected to analyse Br.

c) Influence of matrix effects on LOD.

Table D.1 – Effect of matrix composition on limits of detection of some controlled elements

Element/analyte	Pure polymer	Polymer with ≥ 2 % Sb, without Br	Polymer with ≥ 2 % Br, without Sb
Cadmium	A	~ A → 2A	≥2A
Lead	B	~ 2B	≥3B

NOTE 1 If A and B are limits of detection (LOD) for Cd and Pb, respectively, in a pure polymer, then the LODs to be expected for more complex matrices are expressed as multiples of A and B as in Table D.1.

NOTE 2 The information in Table D.1 is provided as guidance only; the actual LODs for the target analytes are specific for each instrument and analytical conditions/parameters employed.

D.3 Interpretation of results

For each analyte the analyst shall prepare an uncertainty budget with an estimate of the expanded uncertainty, U, expressed at a chosen confidence level. Using the value for U and the maximum allowed level, L, of the substance, the analyst shall categorize each sample as:

a) "BELOW LIMIT" – If the results, R_i, of the quantitative analysis for all analytes are lower than the values, P_i, calculated by Equation (D.1), the result for the sample is "BELOW LIMIT".

$$P_i = L_i - U_i \quad \text{(D.1)}$$

where "i" indicates each analyte.

b) "OVER LIMIT" – If the results, R_i, of the quantitative analysis for any individual analyte is higher than the values, F_i, calculated from Equation (D.2), the result for the sample is "OVER LIMIT".

$$F_i = L_i + U_i \quad \text{(D.2)}$$

NOTE 1 In case of actual legislation, which restricts PBB/PBDE and Cr(VI) rather than Br and Cr, the exceptions are the XRF determinations of Br and Cr. If the quantitative results for the elements Br and/or Cr are higher than the limit (for Br calculated based on the stoichiometry of Br in the most common congeners of PBB/PBDE), the sample is "inconclusive", and even if the quantitative results for all other analytes are "below limit".

c) "INCONCLUSIVE" – If the result, R_i, of the quantitative analysis for any individual analyte in a sample is intermediate between P_i and F_i, the test is "INCONCLUSIVE" for that sample.

- The value L is defined by the restrictions being used to judge the acceptability of the material in the product. If the material listed in the governing restrictions is in the elemental form, L shall be used directly from the governing restrictions. If the material listed in the governing restrictions is in compound form, the value for L shall be

calculated using the gravimetric factor for the element being determined using XRF in the target chemical compound.

– The value *U* above denotes an estimate of the uncertainty associated with the XRF determination of each analyte. That is, *U* is different for each combination of analyte, sample preparation procedure, calibration, and spectrometer. Guidance on the estimation of uncertainty may be obtained from ISO/IEC Guide 98.

NOTE 2 The user may choose a value to substitute for *U* on the basis of a desired margin of safety. However, it is recommended that efforts be made to estimate *U* to ensure that it is less than or equal to the chosen safety margin.

d) Example scheme for interpreting results at sample limits are given in Table D.2.

Table D.2 – Screening limits in mg/kg for regulated elements in various matrices

Element	Polymers	Metals	Composite material
Cd	BL ≤ (70-3σ) < X < (130+3σ) ≤ OL	BL ≤ (70-3σ) < X < (130+3σ) ≤ OL	LOD < X < (150+3σ) ≤ OL
Pb	BL ≤ (700-3σ) < X < (1 300+3σ) ≤ OL	BL ≤ (700-3σ) < X < (1 300+3σ) ≤ OL	BL ≤ (500-3σ) < X < (1 500+3σ) ≤ OL
Hg	BL ≤ (700-3σ) < X < (1 300+3σ) ≤ OL	BL ≤ (700-3σ) < X < (1 300+3σ) ≤ OL	BL ≤ (500-3σ) < X < (1 500+3σ) ≤ OL
Br	BL ≤ (300-3σ) < X		BL ≤ (250-3σ) < X
Cr	BL ≤ (700-3σ) < X	BL ≤ (700-3σ) < X	BL ≤ (500-3σ) < X

– A common set of limits for the substances of interest have been assumed for the purposes of this example. The limits are 100 mg/kg for Cd and 1 000 mg/kg for Pb, Hg and Cr. The limit for Br is calculated based on the stoichiometry of Br in the most common congeners of PBB/PBDE and their limit of 1 000 mg/kg. The “action levels” for this method have been set for the purpose of this screening procedure with a 30 % margin of safety (50 % for composite materials).

– A “BELOW LIMIT” (BL) or “OVER LIMIT” (OL) determination will be set at 30 % (50 % for composite materials) less than or greater than the limit, respectively. The margins of safety have been agreed upon based on the experience of many experts and practitioners in the industry. Further explanation of this approach to estimating uncertainty (translated here as “margin of safety”) can be found in 6.6 c).

– The symbol “X” marks the region where further investigation is necessary.

– The term “3σ” expresses the repeatability of the analyser at the action level, where σ is determined as the standard deviation of a typical sample with the content of the regulated substances near the limits of interest (see spectrometer performance verification test 6.5.4). The repeatability is expressed in terms of “3σ” 99,7 % confidence level rather than the more common “2σ” 95 % confidence level. The 99,7 % confidence level will allow the method to produce fewer “false negative errors”.

NOTE 3 The limit of detection of the instrument should be below the “action level” and should be applied in accordance with the note in 6.5.4 d).

D.4 Summary results of the IIS2 as related to the XRF method

Volunteer laboratories chosen by IEC TC111 WG3 participated in an international inter-laboratory study (IIS2) to determine the performance of this test method. The CRMs (certified reference materials) that were donated were research samples of known composition, and real samples were analysed as per procedures described in this clause. The equipment used in these tests ranged from laboratory ED-XRF or WD-XRF, through bench-top to portable and hand-held XRF analysers. Samples were analysed “as is”. All samples were assumed to be homogeneous, although this assumption has been validated only for CRM samples. The most questionable was homogeneity of samples of ground printed wiring board (F20 and F21).

Tables D.3 to D.7 present a detailed summary of the results for each substance and material tested, obtained for the purposes of evaluating this XRF method. These results support the conclusions about the method (XRF) performance formulated in 6.7.

Table D.3 – Mean results and recovery rates for lead obtained in the IIS2 study

Sample number	Sample description	Certified value of Pb mg/kg	Mean result of Pb mg/kg	Standard deviation mg/kg	Recovery rate[a] %	Range of recovery rate %	Total number of data sets[b]	Number of data sets used[b]
IIS2-C10	EC 680 (polyethylene)	107,9	115	20	107	91 – 152	10	10
IIS2-C11	EC 681 (polyethylene)	13,8	18	10	132	92 – 278	10	8
IIS2-C12	NMIJ CRM 8112-a (acrylonitrile butadiene styrene)	108,9	95	15	87	66 – 110	13	12
IIS2-C13	NMIJ CRM 8113-a (acrylonitrile butadiene styrene)	1 084	952	156	88	67 – 106	13	12
IIS2-F22	BCR 126 (lead crystal glass)	240 000	232 192	58 270	97	62 – 129	5	4
IIS2-D14	NIST SRM 2166 (low alloy steel)	30	ND[c]				5	0
IIS2-D15	NIST SRM 855a (aluminium casting alloy)	190	187	50	98	64 – 122	6	3
IIS2-D16	NIST SRM 87a (silicon aluminium alloy)	930	1 021	269	110	73 – 150	11	7
IIS2-D18	MBH CRM 74X CA4 (tin-based alloy)	174	ND[c] (ranged from 60 to 377)				9	4
IIS2-F20	Real sample (ground PWB)	23 000	18 735	5 897	81	54 – 87	6	4
IIS2-F21	Real sample (ground PWB)	22 000	7 991	1 931	36	23 – 44	5	4

[a] Recovery rate is defined as the ratio of the actually measured concentration of analyte to the expected one and multiplied by 100 %. In other words, it illustrates inaccuracy of the results.

[b] Each data set typically represents three replicate analyses of the sample.

[c] ND means “not detected”.

Table D.4 – Mean results and recovery rates for mercury obtained in the IIS2 study

Sample number	Sample description	Certified value of Hg mg/kg	Mean result of Hg mg/kg	Standard deviation mg/kg	Recovery rate[a] %	Range of recovery rate %	Total number of data sets[b]	Number of data sets used
IIS2-C10	EC 680 (polyethylene)	25,3	25	11	100	0 - 146	10	8
IIS2-C11	EC 681 (polyethylene)	4,5	4	3	89	0 - 133	10	5
IIS2-C12	NMIJ CRM 8112-a (acrylonitrile butadiene styrene)	100	92	15	92	67 - 117	13	12
IIS2-C13	NMIJ CRM 8113-a (acrylonitrile butadiene styrene)	941,5	893	109	95	80 - 120	13	12

[a] Recovery rate is defined as the ratio of the actually measured concentration of analyte to the expected one and multiplied by 100 %. In other words it illustrates inaccuracy of the results.

[b] Each data set typically represents three replicate analyses of the sample.

Table D.5 – Mean results and recovery rates for cadmium obtained in the IIS2 study

Sample number	Sample description	Certified value of Cd mg/kg	Mean result of Cd mg/kg	Standard deviation mg/kg	Recovery rate[a] %	Range of recovery rate %	Total number of data sets[b]	Number of data sets used
IIS2-C10	EC 680 (polyethylene)	140,8	133	19	94	78 – 116	10	9
IIS2-C11	EC 681 (polyethylene)	21,7	20	5	91	65 – 124	10	9
IIS2-C12	NMIJ CRM 8112-a (acrylonitrile butadiene styrene)	10,77	16	13	155	90 – 500	13	10
IIS2-C13	NMIJ CRM 8113-a (acrylonitrile butadiene styrene)	106,9	92	13	86	72 – 111	13	9
IIS2-D18	CRM “MBH” (tin-based alloy)	3,3	ND[c]				8	0

[a] Recovery rate is defined as the ratio of the actually measured concentration of analyte to the expected one and multiplied by 100 %. In other words it illustrates inaccuracy of the results.

[b] Each data set typically represents three replicate analyses of the sample.

[c] ND means “not detected”.

Table D.6 – Mean results and recovery rates for total chromium obtained in the IIS2 study

Sample number	Sample description	Certified value of Cr mg/kg	Mean result of Cr mg/kg	Standard deviation mg/kg	Recovery rate[a] %	Range of recovery rate %	Total number of data sets[b]	Number of data sets used
IIS2-C10	EC 680 (polyethylene)	114,6	134	38	117	61 – 182	10	10
IIS2-C11	EC 681 (polyethylene)	17,7	20	6	112	68 – 185	10	7
IIS2-C12	NMIJ CRM 8112-a (acrylonitrile butadiene styrene)	27,87	125[c]	42	448		13	13
IIS2-C13	NMIJ CRM 8113-a (acrylonitrile butadiene styrene)	269,5	1 016[c]	303	377		13	13
IIS2-F22	BAM S004 (glass)	94	77	32	82	50 – 110	3	2
IIS2-D14	SRM 2166 (low alloy steel)	240	ND[d] (ranged from ND to 827)				5	0
IIS2-D15	SRM 855a (aluminium casting alloy)	130	ND[d] (ranged from 89 to 890)				5	0
IIS2-D16	SRM 87a (silicon aluminium alloy)	1 100	1 107	450	110	55 – 152	11	4

[a] Recovery rate is defined as the ratio of the actually measured concentration of analyte to the expected one and multiplied by 100 %. In other words it illustrates inaccuracy of the results.

[b] Each data set typically represents three replicate analyses of the sample.

[c] The underlined results for samples C12 and C13 are for information only. In both samples the Cr results reported by the laboratories were a factor of about four larger than certified. The reason for this has not been established.

[d] ND means “not detected”.

Table D.7 – Mean results and recovery rates for total bromine obtained in the IIS2 study

Sample number	Sample description	Certified value of Br	Mean result of Br	Standard deviation	Recovery rate[a]	Range of recovery rate	Total number of data sets[b]	Number of data sets used
		mg/kg	mg/kg	mg/kg	%	%		
IIS2-C10	EC 680 (polyethylene)	808	826	90	102	70 – 125	10	8
IIS2-C11	EC 681 (polyethylene)	98	90	13	92	65 - 102	10	8
IIS2-A01	HIPS (high-impact polystyrene), donated research sample	99 138	104 976	15 353	105	84 – 124	12	5
IIS2-A02	HIPS (high-impact polystyrene), donated research sample	100 050	116 007	10 053	116	100 – 125	12	5
IIS2-A03	ABS (acrylonitrile butadiene styrene), donated research sample	116 800	118 817	29 351	102	69 – 123	6	5
IIS2-A04	ABS (acrylonitrile butadiene styrene), donated research sample	118 400	127 856	32 346	108	90 – 131	6	5
IIS2-A05	PC/ABS (polycarbonate and acrylonitrile butadiene styrene), donated research sample	800	995	90	124	114 – 136	4	3
IIS2-A06	PC/ABS (polycarbonate and acrylonitrile butadiene styrene), donated research sample	2 400	3 034	467	126	111 – 148	4	3

[a] Recovery rate is defined as the ratio of the actually measured concentration of analyte to the expected one, and multiplied by 100 %. In other words it illustrates inaccuracy of the results.

[b] Each data set typically represents three replicate analyses of the sample.

Annex E
(informative)

Practical application of determination of mercury in polymers, metals and electronics by CV-AAS, CV-AFS, ICP-OES and ICP-MS

E.1 Equipment

Below is an example of the equipment used.

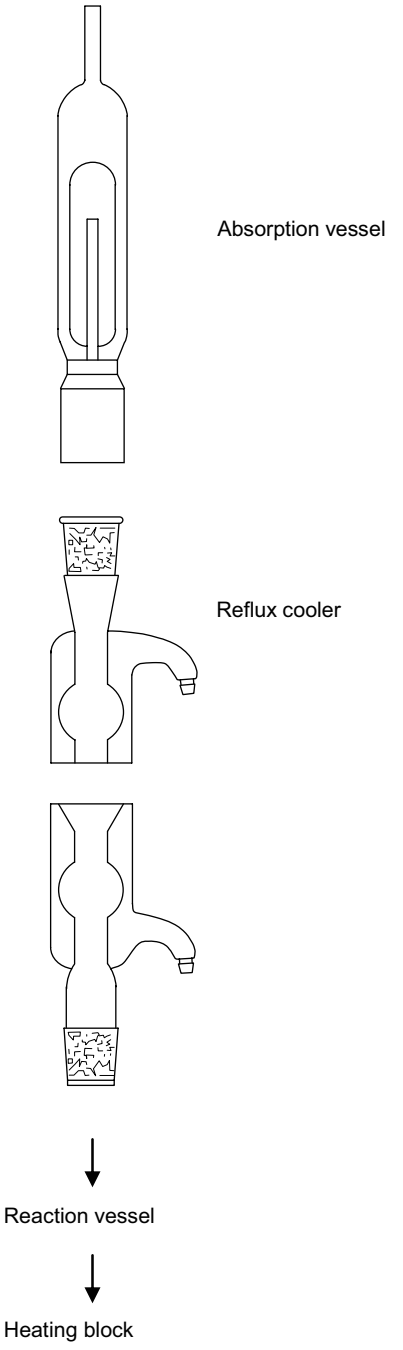

Figure E.1 – Heating digester equipped with reaction vessel, reflux cooler and absorption vessel

Table E.1 – Program for microwave digestion of samples (power output for five vessels)

Step	Time min	Power output W	Pressure limited to MPa
1	5	400	3,5
2	5	600	3,5
3	12	800	3,5
4	20	800	4,0
5	3	500	4,0
Ventilation step	20	0	–

E.2 Instrument parameters

The listed instrument parameters are examples of workable instrument parameters and may differ, since individual instruments may require alternate parameters. The use of listed wavelengths and mass-charge ratios is highly recommended; the selection of other parameters in this context can cause false results.

a) CV-AAS
   - Light source: Electrodeless discharge lamp or hollow cathode lamp
   - Wavelength: 253,7 nm
   - Spectral bandwidth: 0,7 nm
   - Purge gas: N_2 or Ar

b) CV-AFS
   - Source: Hg hollow cathode lamp, current: 30 mA, wavelength: 253,7 nm
   - Detector bias voltage: -360 V
   - Oven temperature: 800 °C
   - Ar flow carrier gas: 0,6 l/min, screen gas: 1,0 l/min
   - Wash water: 6 % (m/m) HNO_3

c) ICP-OES
   - Hg wavelength: 194,227 nm
   - RF generator power: 1 150 W
   - Frequency of RF generator: 27,12 MHz
   - Ar pressure: 0,16 MPa
   - Ar flow carrier gas: Cool gas: 14 l/min, auxiliary gas: 0,5 l/min
   - Sample uptake rate: 1,6 ml/min

d) ICP-MS
   - Mass-charge ratios for Hg: m/z = 199, 200, 201, 202
   - RF generator power: 1 200 W
   - Frequency of RF generator: 27,12 MHz
   - Ar pressure: 0,28 MPa
   - Ar flow carrier gas: Cooling gas: 16 l/min, auxiliary gas: 1,0 l/min

NOTE Torch position: sampling depth, horizontal, vertical; lenses: all conditions should be optimized before measurement.

Annex F
(informative)

Practical application of determination of lead and cadmium in polymers by ICP-OES, ICP-MS and AAS

F.1 ICP-OES

Table F.1 – Spectral interferences for the wavelengths of cadmium and lead

	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 F.1 *(continued)*

	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 The table 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).								

F.2 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. If the sample contains tin or molybdenum, attention shall be paid to positive interference in cadmium mass measurement.

Table F.2 – 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

F.3 AAS

Recommended measurement wavelengths for AAS.

Table F.3 – 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

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

Annex G
(informative)

Practical application of determination of lead and cadmium in metals by ICP-OES, ICP-MS and AAS

G.1 ICP-OES

Table G.1 – Spectral interferences for the wavelengths of cadmium and lead

	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	-	-	-	-	-	+	-	+++
Ta	-	-	-	-	-	+	-	++

Table G.1 *(continued)*

	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**
Pb	+	+	+	+	-	-	-	-
Cd	-	-	-	-	+	+	+	+

NOTE The table 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).

G.2 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 G.1 shows an example of the effect of background correction. Figure G.1a shows an example of uniform background versus wavelength. In this case, the background could be corrected by both positions A and B. Figure G.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.

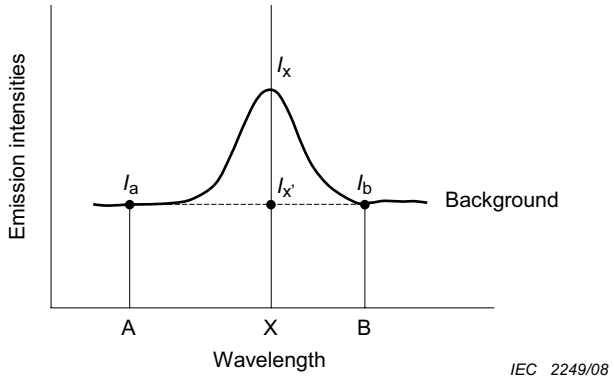

Figure G.1a – Uniform background versus wavelength

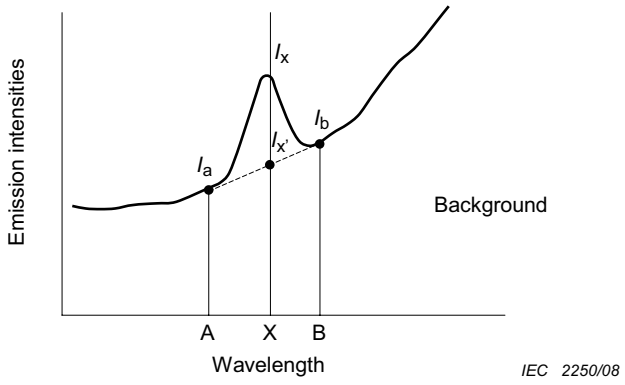

Figure G.1b – Changing background versus wavelength

Figure G.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.

G.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. If the sample contains tin or molybdenum, attention shall be paid to positive interference in cadmium mass measurement.

Table G.2 – 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

G.4 AAS

Recommended measurement wavelengths for AAS.

Table G.3 – Examples for 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

Annex H
(informative)

Practical application of determination of lead and cadmium in electronics by ICP-OES, ICP-MS and AAS

H.1 Program for microwave digestion

Table H.1 – 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.			

H.2 ICP-OES

Table H.2 – Spectral interferences for the wavelengths of cadmium and lead

	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	-	-	-	-	-	+	-	+++
Ta	-	-	-	-	-	+	-	++

Table H.2 *(continued)*

	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**
Pb	+	+	+	+	-	-	-	-
Cd	-	-	-	-	+	+	+	+
NOTE The table 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).								
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H.3 Background correction

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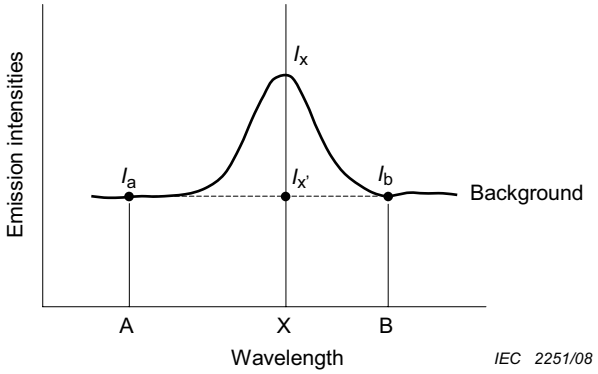

Figure H.1a – Uniform background versus wavelength

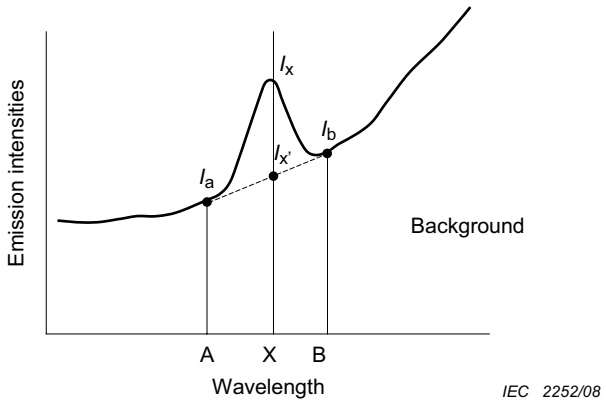

Figure H.1b – Changing background versus wavelength

Figure H.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.

H.4 ICP-MS

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

Table H.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

H.5 AAS

Recommended measurement wavelengths for AAS.

Table H.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

Gas type: Acetylene/air.

Light source: Electrodeless discharge lamp or hollow cathode lamp.

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[53] United States Environmental Protection Agency (EPA), EPA method 7196A, "Chromium, Hexavalent (colorimetric)", July 1992

[54] ZVO-0102-QUA-02, Qualitative Analysis of Cr-VI in Passivation Layers on Parts by Spot Analysis

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