



BSI British Standards

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

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National foreword

This British Standard is the UK implementation of EN 62321:2009. It is identical to IEC 62321:2008.

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

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

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EUROPEAN STANDARD
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EN 62321

April 2009

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English version

**Electrotechnical products -
Determination of levels of six regulated substances
(lead, mercury, cadmium, hexavalent chromium,
polybrominated biphenyls, polybrominated diphenyl ethers)
(IEC 62321:2008)**

Produits électrotechniques -
Détermination des niveaux
de six substances réglementées
(plomb, mercure, cadmium, chrome
hexavalent, diphényles polybromés,
diphényléthers polybromés)
(CEI 62321:2008)

Produkte in der Elektrotechnik -
Bestimmung von Bestandteilen
der sechs Inhaltsstoffe
(Blei, Quecksilber, Cadmium,
sechswertiges Chrom, polybromiertes
Biphenyl, polybromierter Diphenylether),
die einer Beschränkung unterworfen sind
(IEC 62321:2008)

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CENELEC

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

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Foreword

The text of document 111/116/FDIS, future edition 1 of IEC 62321, prepared by IEC TC 111, Environmental standardization for electrical and electronic products and systems, was submitted to the IEC-CENELEC parallel vote and was approved by CENELEC as EN 62321 on 2009-03-01.

The following dates were fixed:

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Annex ZA has been added by CENELEC.

Endorsement notice

The text of the International Standard IEC 62321:2008 was approved by CENELEC as a European Standard without any modification.

In the official version, for Bibliography, the following notes have to be added for the standards indicated:

IEC 60730-1	NOTE Harmonized as EN 60730-1:2000 (modified).
ISO 3613	NOTE Harmonized as EN ISO 3613:2001 (not modified).
ISO 17294-1	NOTE Harmonized as EN ISO 17294-1:2006 (not modified).

Annex ZA (normative)

Normative references to international publications with their corresponding European publications

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.

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

<u>Publication</u>	<u>Year</u>	<u>Title</u>	<u>EN/HD</u>	<u>Year</u>
ISO/IEC Guide 98	1995	Guide to the expression of uncertainty in measurement (GUM)	-	-
ISO/IEC 17025	- ¹⁾	General requirements for the competence of testing and calibration laboratories	EN ISO/IEC 17025	2005 ²⁾
ISO 3696	- ¹⁾	Water for analytical laboratory use - Specification and test methods	EN ISO 3696	1995 ²⁾
ISO 5961	- ¹⁾	Water quality - Determination of cadmium by atomic absorption spectrometry	EN ISO 5961	1995 ²⁾

¹⁾ Undated reference.

²⁾ Valid edition at date of issue.

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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 disjointment¹.

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*

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 : <i>Bureau Communautaire de Référence</i>)
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.

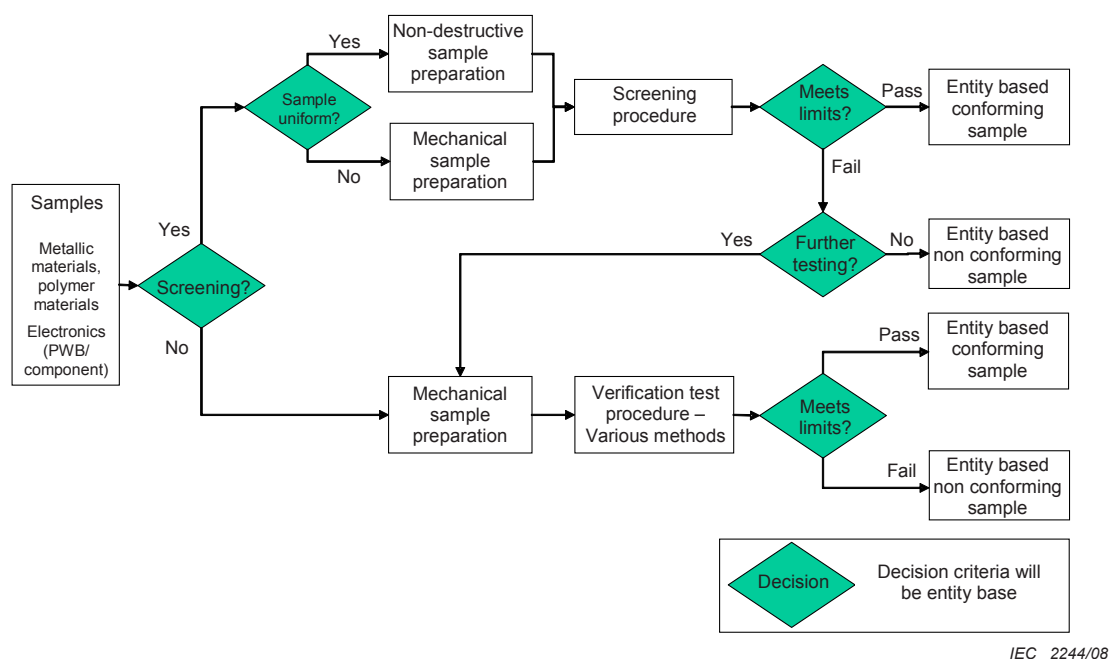


Figure 1 – Flow chart of the test methods

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 LN₂ 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 (LN₂).

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 LN₂).

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 LN₂ (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 LN₂ (5.2.j). Wait until the LN₂ (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 LN₂ (5.2.j) if needed. For organic samples that have no metal parts, cryogenic milling is recommended. Be careful not to allow the LN₂ (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 LN₂ (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. BrK α on PbL α or AsK α on PbL α 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 α_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:

$$\text{LOD} = 3\sigma \quad (1)$$

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:

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

- 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:

- 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).
- 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.
- 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 ICP-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 polyether (PFPE).

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): $\rho(\text{HNO}_3) = 1,4 \text{ g/ml}$, 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 borohydride): 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) NaBH₄ 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) KBH₄ 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.