Title: IEC 62321, Ed.1: Procedures for the determination of levels of six regulated substances (Lead, Mercury, Cadmium, Hexavalent Chromium, Polybrominated Biphenyls, Polybrominated Diphenyl Ethers) in electrotechnical products

Introductory note
Global legislation dealing with hazardous substances is forcing the electrotechnical industry to develop methods for analytical testing of its products. The CDV has addressed all of the comments received by the NCs (from 111/32A/CC) and has also adjusted the scope according to 111/48/INF. An International Interlaboratory Study (IIS) with over 25 labs all over the world is planned by TC 111/WG 3 to assure applicability and practicability of the described procedures. A document describing the results of the IIS will be issued by WG 3 by June 2006.

Note d'introduction
La législation globale s'occupant des substances dangereuses force l'industrie électrotechnique de développer des méthodes d'essais analytiques de ses produits. Le CDV a introduit les commentaires reçus des CNs (111/32A/CC) et a également revu le domaine selon 111/48/INF.

Une étude de laboratoire (IIS) sur plus de 25 labs du monde entier est planifiée par le TC 111/WG3 afin d'assurer l'applicabilité et la faisabilité des procédures décrites. Un document décrivant les résultats de ce IIS sera circulé par le WG3 d'ici Juin 2006.
Procedures for the Determination of Levels of Six Regulated Substances (Lead, Mercury, cadmium, Hexavalent Chromium, Polybrominated Biphenyls, Polybrominated Diphenyl Ethers) in Electrotechnical Products

IEC TC 111 Working Group 3
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Procedures for the Determination of Levels of Six Regulated Substances (Lead, Mercury, Hexavalent Chromium, Polybrominated Biphenyls, Polybrominated Diphenyl Ethers) in Electrotechnical Products

FOREWORD

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

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

<table>
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<th>Report on voting</th>
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<tr>
<td>XX/XX/FDIS</td>
<td>XX/XX/RVD</td>
</tr>
</tbody>
</table>

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 the ISO/IEC Directives, Part 2.
The committee has decided that the contents of this publication will remain unchanged until the maintenance result date\textsuperscript{1}) 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.

\textsuperscript{1}) The National Committees are requested to note that for this publication the maintenance result date is ....
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 like lead (Pb), mercury (Hg), cadmium (Cd), hexavalent chromium (Cr VI) and their compounds, and two types of brominated flame retardants (polybrominated biphenyls, PBB, polybrominated diphenyl ethers, PBDE, except decabrominated diphenyl ether, DecaBDE) in electrotechnical products is regulated in current and proposed regional legislation.

Industry is convinced of the importance of defining testing protocols for regulated substances of electrotechnical products that enter or are made available on markets, where legislation regulating the substance content of electrotechnical product is enacted. Testing may be performed for a variety of reasons including:

- As a supplement to supply chain material declarations, companies may choose to test products directly to determine compliance
- Companies may require their suppliers to perform testing as a supplement to the supplier's material declaration
- Companies may perform “spot checks” of their suppliers to confirm compliance
- Government officials may test as basis to assess compliance

Certain test procedures to determine regulated material content already exist, but most are not appropriate for testing electrotechnical products and are not internationally recognized. Currently no procedures for compliance or enforcement of the substance restrictions have been agreed upon or mandated by countries regulating substances in electrotechnical products. Testing procedures, which are being discussed by industry associations and academia to determine presence and levels of these banned substances differ from each other.

Until a common agreement between governments, industry and other stakeholders is reached on how regulated substances should be measured in electrotechnical products, industry has no legal certainty that products will be found compliant if tested by national enforcement authorities or by Non Governmental Organizations (NGOs) in different countries.

The purpose of this standard is therefore to provide test procedures as one option that will allow the electrotechnical industry to determine the levels of the regulated substances Pb, Hg, Cd, Cr VI and their compounds and PBB, PBDE (except decabrominated diphenyl ether, DecaBDE) in electrotechnical products on a consistent global basis.
Procedures for the Determination of Levels of Six Regulated Substances (Lead, Mercury, Cadmium, Hexavalent Chromium, Polybrominated Biphenyls, Polybrominated Diphenyl Ethers) in Electrotechnical Products

1 Scope

This document provides test procedures for determining the levels of lead (Pb), mercury (Hg), cadmium (Cd), hexavalent chromium (Cr VI) and their compounds, and two types of brominated flame retardants, polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE) (except decabrominated diphenyl ether, DecaBDE), contained in electrotechnical products.

NOTE: Although not regulated, DecaBDE is referenced in this standard at a few instances for informative purposes with regards to technical aspects.

This document refers to the sample as the object to be processed and measured. What the sample is or how to get to the sample is defined by the entity carrying out the procedures. A general guidance to obtain representative samples from finished electronic products to be tested for the determination of levels of regulated substances is given in Annex A of this standard.

It is noted that the selection and/or determination of the sample may affect the interpretation of the test results.

This document will not determine:

- Definition of a “unit” or “homogenous material” as the sample
- Disassembly procedure to get to a sample
- Assessment procedures

2 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.

ASTM C 982-03, Guide for Selecting Components for Energy-Dispersive X ray Fluorescence Systems

ASTM C 1118-89, Guide for Selecting Components for Wavelength-Dispersive X ray Fluorescence Systems

ASTM E 1172-87, Standard Practice for Describing and Specifying a Wavelength-Dispersive X-Ray Spectrometer

ASTM D 1498-93, Standard Practice for Oxidation Reduction Potential of Water

ASTM E 1361-02, Guide for Correction of Interelement Effects in X ray Spectrometric Analysis


ASTM E 1622-94, Standard Practice for Correction of Spectral Line Overlap in Wavelength-Dispersive X-Ray Spectrometry

ASTM D 4004-93, Standard Test Methods for Rubber-Determination of Metal Content by Flame Atomic Absorption (AAS) Analysis
DIN 50993-1, *Determination of hexavalent chromium in corrosion protection coatings - Part 1: Qualitative analysis*

EN 1122, *Plastics – Determination of cadmium – Wet decomposition method*

EN 13346, *Characterization of sludges – Determination of trace elements and phosphorus – Aqua regia extraction methods*

ISO 247, *Rubber – Determination of ash*

ISO 3613, *Chromate conversion coatings on zinc, cadmium, aluminium-zinc alloys and zinc-aluminium alloys – Test methods*

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

ISO 3856-4, *Paints and varnishes; Determination of "soluble" metal content; Part 4 : Determination of cadmium content; Flame atomic absorption spectrometric method and polarographic method*

ISO 5725, *Accuracy (trueness and precision) of measurement methods and results*

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

ISO 11885, *Water quality - Determination of 33 elements by inductively coupled plasma atomic emission spectrometry*

ISO 17025, *General Requirements for the Competence of Testing and Calibration Laboratories*

ISO 17294-1, *Water quality- Application of inductively coupled plasma mass spectrometry (ICP-MS) for the determination of elements – Part1: General guidelines*

JIS K 0102, *Testing methods for industrial wastewater*

JIS K 0116, *General rules for atomic emission spectrometry*

JIS K 0133, *General rules for high frequency plasma mass spectrometry*

### 3 Definitions

For the purpose of this International Standard, the following definitions apply.

#### 3.1 Analyte
substance to be measured

#### 3.2 Calibrant
see 3.3 Calibration standard

#### 3.3 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)
3.4 Calibration blank
substance identical in form and matrix composition to the calibration standard(s) but containing no analyte(s)

3.5 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]

3.6 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 [IEC 60730-1, ed. 3.0 (1999-04)]
EXAMPLE group of components mounted on a printed circuit board.

3.7 Electronic component
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 [IEC 62239, ed. 1.0 (2003-05)]
EXAMPLE Resistors, capacitors, diodes, integrated circuits, hybrids, application specific integrated circuits, wound components and relays.

3.8 Electronics
electronic assembly and/or electronic component and/or field replaceable unit

3.9 Field replaceable unit (FRU)
part, component or subassembly that is easily removed (mechanically disjointed) using ordinary tools [IEC Guide 114]
NOTE “Easily removed” consists of using ordinary tools to perform such functions as screwing or disconnecting, and only without irreversibly destroying the unit.

3.10 Matrix
material or substance and its form or state in which analyte is embedded or to which analyte is attached.

3.11 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]

3.12 Abbreviations
AAS Atomic Absorption Spectrometry
ABS Acrylonitrile Butadiene Styrene
AFS Atomic Fluorescence Spectrometry
ASTM American Society for Testing and Materials
CCC Calibration Check Standard
CRM Certified Reference Material
CV-AAS Cold Vapor Atomic Absorption Spectrometry
DecaBDE  Decabrominated Diphenyl Ether
DI     De-ionized (water)
DIN    Deutsches Institut für Normung
EDXRF  Energy Dispersive X-Ray Fluorescence
EEE    Electrical and Electronic Equipment
EI     Electron Ionization
EN     European Norm
EPA    Environmental Protection Agency
FEP    Fluorinated Ethylene-Propylene Copolymer
FP     Fundamental Parameters
FRU    Field Replaceable Unit
GC-MS  Gas Chromatography - Mass Spectrometry
GLP    Good Laboratory Practice
HDPE   High-Density Polyethylene
HPLC-UV High-Performance Liquid Chromatography - Ultra Violet
HIPS   High-Impact Polystyrene
IC     Integrated Circuit
ICP-OES Inductively Coupled Plasma Optical Emission Spectrometry
ICP-MS Inductively Coupled Plasma Mass Spectrometry
IS     Internal Standard
JIS    Japanese Industrial Standard
LLOD   Low Limits of Detection
MDL    Method Detection Limit
NMIJ   National Metrology Institute of Japan.
OctaBB Octabromobiphenyl
OctaPBD Octabromo Diphenyl Ether
PBB    Polybrominated Biphenyl
PBDE   Polybrominated Diphenyl Ether
PC     Polycarbonate
PCB    Polychlorinated Biphenyl
PCT    Polychlorinated Terphenyl
PCN    Polychlorinated Naphthalene
PFA    Perfluoroalkoxy
PFN    Perfluorokerosene
PFTBA  Perfluorotributylamine
PTFE   Polytetrafluoroethylene
PTV    Programmable Temperature Vaporization (injector)
PVC    Polyvinyl Chlorid
PWB    Printed Wiring Board
QA     Quality Assurance
QC     Quality Control
SIM    Single Ion Monitoring
WDXRF  Wavelength dispersive X-ray fluorescence
4 Test Procedure Overview

4.1 Test Procedure Scope

The content of the test procedures to determine the levels of regulated substances is grouped in two important steps:

- Analytical test procedures
- Laboratory implementation

Analytical test procedures are developed and validated to make sure they are suitable and can be used for the purpose they were designed for. Subsequently they have to be made available to the public so that interested parties around the globe can implement them.

The analytical test procedures are divided into seven important points:

- Scope, application and summary of method
- Apparatus / Equipment and materials
- Reagents
- Sample preparation
- Test procedure, which includes:
  - Calibration
  - Instrument performance
  - Sample analysis
  - Calculation of analytical results
  - Test report
  - Quality control

Individual test procedure descriptions in clauses 5 to 13 follow this five point outline.

The laboratory implementation is not covered in this standard, as labs are able to implement the test procedures described using procedures 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 instrument in the lab. Quality assurance systems such as Good Laboratory Practice (GLP) and/or accreditation to similar (inter-) national systems (e.g. ISO 17025) are strongly encouraged.

4.2 Sample

This document refers to the sample as the object to be processed and measured according to the procedures to determine the levels of the regulated substances. A sample can either be a polymer, a metal, or electronics (electronic component, electronic assembly, or field replaceable unit).

What the sample is or how to get to the sample is defined by the entity carrying out the procedures.

The entity may decide to prepare a sample which is a homogenous material. For this kind of sample the procedures offered for metals or polymers are especially suited.

NOTE: The European Commission has given the following guidance on homogenous materials: "A material that can not be mechanically disjointed into different materials (Frequently Asked Questions on RoHS and WEEE). Further definitions are given as follows: The term "homogeneous" means "of uniform composition throughout". Examples of "homogeneous materials" are individual types of: plastic, ceramics, glass, metals, alloys, paper, board, resins, and..."
coatings. The term “mechanically disjointed” means that the materials can, in principle, be separated by mechanical actions such as: unscrewing, cutting, crushing, grinding and abrasive processes.

The entity may also decide to prepare a sample which is an electronic component or an electronic assembly or a field replaceable unit (FRU). For this kind of sample the procedures offered for electronics are especially suited.

The procedure to obtain the sample is outside of the scope of this document. A general guidance to obtain representative samples from finished electronic products to be tested for the determination of levels of regulated substances is given in the informative Annex A of this standard.

### 4.3 Test Procedure Flow

The figure below describes the flow for the test procedure to determine the levels of regulated substances in electrotechnical products.

![Flowchart of the Test Procedure](image)

**Figure 1: Flowchart of the Test Procedure**

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

The screening test procedure may be carried out either by directly measuring the sample (non-destructive sample preparation) or by destructing 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 plastics, alloys, glass) may be done non-destructively, while for other, more complex samples (like a FRU) mechanical sample preparation is necessary. Mechanical sample preparation is the same for both the screening, as well as for the verification test procedure. The procedure for mechanical sample preparation is described in clause 5.

The screening of a sample is performed using any XRF spectrometer (e.g. EDXRF (Energy Dispersive X-ray Fluorescence) or WDXRF (Wavelength Dispersive X-ray Fluorescence)), providing it has the performance characteristics described in clause 6. It shall be noted that the screening test procedure should be performed under controlled conditions. The XRF analysis technique has limitations to its use and the applicability of the results obtained,
although it’s fast and resource efficient way of analysis has its merits particularly for the demands of the electrotechnical industry.

The verification test procedure is performed after a mechanical sample preparation using a variety of analytical procedures tailored to the regulated substances and the sample, which can be either a polymer, a metal or electronics (in form of electronic components or electronic assemblies). Table 1 gives an overview of the verification methods, which are described in detail in clause 7 to 13. The intent of using a particular verification test procedure is to ensure the most accurate results possible; however, it most likely will take more resources to carry out.

### Table 1: Overview of the content of the verification test procedure

<table>
<thead>
<tr>
<th>Steps</th>
<th>Substances</th>
<th>Polymers</th>
<th>Metals</th>
<th>Electronics (PWBs/Components)</th>
</tr>
</thead>
<tbody>
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<td>Mechanical sample preparation</td>
<td></td>
<td>Direct measurement</td>
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<td></td>
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<td>Dry Ashing</td>
<td>Solvent extraction</td>
<td>Solvent extraction</td>
</tr>
<tr>
<td>Analytical technique definition</td>
<td>PBB/PBDE</td>
<td>GC-MS (Clause 7)</td>
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<td>GC-MS (Clause 7)</td>
</tr>
<tr>
<td>(incl. typical margins of errors)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Cr VI</td>
<td>Alkaline Digestion/</td>
<td>Spot-test procedure/ boiling-water-extraction procedure (Clause 8)</td>
<td>Alkaline Digestion/ Colorimetric Method (Clause 9)</td>
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<tr>
<td></td>
<td>Colorimetric Method (Clause 9)</td>
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<tr>
<td>Hg</td>
<td>CV-AAS, AFS, ICP-OES, ICP-MS, (Clause 10)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb/Cd</td>
<td>ICP-OES, ICP-MS, AAS (Clause 11)</td>
<td>ICP-OES, ICP-MS, AAS (Clause 12)</td>
<td>ICP-OES, ICP-MS, AAS (Clause 13)</td>
<td></td>
</tr>
</tbody>
</table>

After the verification test procedure it should be decided if the sample meets the limits based on the entity's criteria for regulated substances.

### 4.4 Adjustment to Matrix

Analytical procedures for substances that are present at relatively low levels amongst other chemical elements or compounds at relatively high concentrations or representing the major constituent of the sample are very often material or matrix dependent. Therefore the test procedures should 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 with a whole series of additives that can moreover be painted; metals as well as alloys of different types; and electronics such as electrical and electronic components and field replaceable units (FRU).

### 4.5 Laboratory Report

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

a) Name, address and location of any laboratory involved in the analysis and name of the operator
b) Date of receipt of sample and date(s) of performance of test

c) Unique identification of report (such as serial number) and of each page and total number of pages of the report

d) Description and identification of the sample, including a description of any product disassembly performed to acquire the test sample

e) A reference to this IEC standard, the used procedure or performance based equivalent (including digestion method(s) and test instrument(s)).

f) The detection limit or reporting limit

g) The results of the test expressed as milligrams / kilogram (mg/kg) in samples tested

h) Any details not specified in this standard which are optional, and any other factors which may have affected the results. Any deviation, by agreement or otherwise, from the test procedure specified here

Results from all quality assurance and quality control (QA/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 issue shall be made only in a further document suitably marked, e.g. "Amendment/Addendum to test report serial number (or as otherwise identified)“, and shall meet the relevant requirements of the preceding paragraphs.

4.6 Alternative Procedures

Other alternative procedures, digestion methods or analytical techniques may be utilized once the performance effectiveness has been validated according to the performance based measurement system criteria, which are referenced in the Quality Control clauses of the procedures. Any deviation from the described procedures has to be evaluated and documented in the test report.
5 Mechanical Sample Preparation

5.1 Scope, Application and Summary of Method

This clause describes, in general terms, procedures for the mechanical sample preparation of electrotechnical products. Some clauses dealing with specific testing methods have requirements on sample handling in specific situations. In order to allow reproducible measurement results, the sample material should be as uniform as possible (in case of non-uniform materials) and show a consistent grain size distribution and density of the sample (for uniform materials).

The following clauses describe common mechanical particle size reduction techniques. Selection of the appropriate technique(s) is dependent on the required particle size for the test procedure to be employed.

Due to the risk of analytical mistakes from evaporation of volatile components (e.g. volatilization due to heat), loss of material through dust emissions and contamination, it is important to select the appropriate equipment and especially to keep them clean.

Contamination can occur from the grinding equipment itself, which is of considerable concern for the measurement of (heavy) metals. For the equipment used in the mechanical preparation, it must be known which elements can be released to 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) from stainless steel equipment.

Furthermore one should keep in mind that the sample size may have influence on the result of the analysis. One example is the case where leaching behavior may impact the result. Where the sample has a non-homogeneous particle size distribution, the smaller particles have a relatively large area, which may influence the end result.

The laboratory must be able to demonstrate by experiment that the procedure employed for mechanical sample preparation does not directly contribute detectable amounts of interest elements or compromise the specimen to effect loss of those elements. This can be demonstrated experimentally by the milling and analysis of a certified reference material (or other suitably known regulated substance containing test specimen) immediately after a similarly analyzed test specimen known to contain significant levels of regulated substances. Certified Reference Materials are not mandated. The materials used must however have well known regulated substance content to determine that the mechanical grinding/milling/cutting processes is not contributing contamination or causing loss of regulated substances. Continuing demonstration of the mechanical sample preparation procedure effectiveness can be monitored by standard quality control practices including matrix spikes and control samples.

The laboratory must also be able to demonstrate by experiment that the procedure employed for cleaning the mechanical sample preparation equipment prevents contamination of the specimen with interest elements from the previous specimen preparation.

Alternate mechanical sample preparation means can be employed providing that the required sample particle size is achieved without contamination or compromising the sample in relation to the elements of interest.

5.2 Apparatus / Equipment and Materials

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

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

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

d) Homogenizing Mixer

e) Analytical balance: Capable of accurate weighing to 0.0001 g

f) Brushes (different sizes)

g) Paper

h) Scissors, Heavy Plate Shears

i) Glass Beaker

j) Liquid Nitrogen (N₂)

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

k) Powder Funnel

l) Gloves

m) Safety glasses

n) Polyethylene recipient

5.3 Procedure

5.3.1 Sample

The sample to be analyzed must be a uniform material, e.g. a polymer, a metal or electronics. Guidance on how to get to this sample is given in Annex A.

5.3.2 Manual Cutting

Manual cutting is suitable for rough cutting and preparation of samples for further reduction. Samples are precut to a size of no more than 2 × 10 × 10 cm³.

a) Electronics: Samples are precut to a size of 4 x 4 cm² using heavy plate shears.

b) Polymers: Samples are precut to a size of 5 x 5 mm² using heavy plate shears or scissors. Thin polymer foils are to be cut into small pieces with a shear.

5.3.3 Coarse grinding /milling

Coarse grinding is suitable for reduction of samples to ~ 1 mm in diameter. Cool the samples if needed with the liquid nitrogen. For organic samples without metal content, cryogenic milling is recommended. An example of cryogenic preparation is to put the samples in a polyethylene recipient to cool with liquid nitrogen. Time reference is until nitrogen stops boiling and is dissipated and then wait an additional 10 minutes. Then grind samples in mill using 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 with a pre-weighed, 1.0 mm stainless steel bottom sieve and reprocess the 4 mm material. Carefully sweep out the mill and collect all particles. Use a 5 min cooling period between grinding cycles.

5.3.4 Homogenizing

Homogenizing is suitable for preparing the coarsely ground sample in the mixer prior to further size reduction in the centrifugal mill. Use a container with double the capacity of the amount of powder to be mixed. Set the mixer on its middle speed setting by adjusting the drive belts to the center of the drive pulleys. Mix powder until homogeneous.
5.3.5 Fine grinding / milling

Fine grinding or milling is suitable for reduction of samples to < 1 mm in diameter. Cool the homogenized sample powder with the liquid nitrogen, if needed. For organic samples having no metal parts, cryogenic milling is recommended. Be careful not to allow the liquid nitrogen to directly contact the powder to prevent spattering and sample loss, e.g., through usage of polyethylene recipient. Mill the sample powder with the centrifugal mill. Carefully sweep out the centrifugal mill and collect all powder. To ensure a complete homogeneous sample size, sieving can be added.

5.3.6 Very Fine Grinding of Polymers and Organic Materials

This procedure is suitable for reduction of samples as small as 500 µm or less in diameter (not suitable for metal, glass, or similar hard-sharp materials). Approximately 3 g to 10 g of rough-cut (3 mm to 5 mm sections) of material to be ground is placed into the sample tube to about 2/3 to 3/4 full. Add the grinding rod and secure the ends of the vial. Cool the bladeless cryogenic impact grinder from room temperature for 15 min by filling the reservoir with LN₂, placing grinding vials with samples in the mill, locking cover into place. One or more sieves may be added to ensure a complete homogeneous sample size.
6 Screening by X-ray Fluorescence Spectrometry (XRF)

6.1 Scope, Application and Summary of Method

This document describes procedures for the screening analysis of regulated substances found in electro-technical products using the analysis technique of X-ray fluorescence (XRF) spectrometry. It is applicable to polymers, metals, and ceramic materials. The 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 described in this method. Not all types of XRF spectrometers are suitable for all sizes and shapes of sample. Care shall be taken to choose the proper spectrometer design for the task.

This method is designed specifically to screen for lead, cadmium, mercury, chromium, and bromine (Pb, Cd, Hg, Cr, Br) in the basic materials, which comprise most electro-technical products. Under typical circumstances, X-ray fluorescence spectrometry provides information on the total quantity of each element present in the specimen. Generally, the technique is insensitive to chemical composition. Therefore, special attention is needed when determining chromium and bromine, where the result will reflect the total chromium and total bromine present. The presence or absence of hexavalent chromium, PBB, or PBDE shall be confirmed using another test method capable of providing chemical information.

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.

- A universal calibration can be realized 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 calibrants are more 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. Here, a calibration is restricted to a single material matrix with multiple calibrations needed for analyses of multiple 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 specimen may cause a significant bias. Due to the limited availability of calibrants, viz. 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 specimen. In the case of a coating or thin layer, special care shall be taken to ensure the XRF spectrometer has sufficient sensitivity to detect the small quantity of matter in the layer.

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

- Non-destructively - by directly analyzing 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 method will guide the user in choosing the proper approach to sample presentation (see clause 6.10).
6.1.1 Principle

The purpose of this test method is to screen a wide variety of materials for the presence of substances. To achieve this purpose, the method shall provide rapid, unambiguous identification of the elements of interest. The method shall provide at least a level of accuracy that is sometimes described as semi-quantitative. That is, 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 XRF spectrometers cover such a wide range that some will be relatively inadequate in their selectivity and sensitivity and others will be more than adequate. Some spectrometers will allow for easy measurement of a wide range of sample shapes and sizes while other spectrometers will, especially research grade WDXRF units, 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 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 herein in relatively general terms. It is the responsibility of the user to document all procedures developed in the laboratory implementing 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** - Persons using the XRF test methods contained in this standard should be trained in the use of XRF spectrometers and have a working knowledge of the technique and sampling requirements.

**WARNING** - X radiation is dangerous to humans. Care should be taken to operate the equipment in accordance with both safety instructions provided by the manufacturer and applicable local health and occupational safety regulations.

6.2 Apparatus / Equipment and Materials

a) X-ray fluorescence spectrometer - Consists of an X-ray excitation source, means of reproducible sample presentation, X-ray detector, data processor, and control system.

   — Source of X-ray excitation - X-ray tube or radioisotope sources are commonly used.

   — X-ray detector (detection sub-system) - Device used to convert the energy of an X-ray photon into a corresponding electric pulse of amplitude proportional to the photon energy.

6.3 Reagents

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. That is, all grinding materials, solvents, fluxes, etc. shall not contain detectable quantities of Cr, Br, Cd, Hg, and Pb.
Tools used in the handling of specimens shall be chosen to minimize contamination of specimens with the analytes of this test method as well as with any other elements.

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 via either a nondestructive approach in which the portion to be measured is defined by the viewing area of the spectrometer or 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

a) The user shall 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 material other than the defined test portion.

b) The user shall make every effort to establish a repeatable measurement geometry with repeatable distance between the spectrometer and the test portion.

c) The user shall take all practical steps to identify a test portion with as regular shape as possible in consideration of flatness across the entire area, surface roughness, and known physical structure.

d) The user shall document steps taken to disassemble a larger object to obtain a test portion.

6.4.2 Destructive Approach

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

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

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

d) A procedure that results in a material dissolved in a solid matrix shall control and document the quantity and physical characteristics of the material to be dissolved. The resulting solid (fused or pressed pellet) shall be completely homogeneous. Instructions shall be provided to deal with un-dissolved portions to ensure proper interpretations of 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 method will be applied.

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 very small area or very thin specimens. As a consequence, it is imperative the user carefully
establish and clearly document the performance of the test method as implemented in their facility. One goal is to prevent false negative test results.

6.5.2 Preparation of the Spectrometer

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

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

NOTE: Many instruments available on the market are already optimized and preset for particular application and therefore, this step is not necessary. Otherwise, the laboratory shall establish optimum operating conditions for each calibration. Choices shall 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 X-ray lines is given in Table 2. Detection system settings shall optimize the compromise between sensitivity and resolution. Typically, guidance may be found in the instrument manual and in literature on X-ray spectrometry.

6.5.3 Test Portion

a) The creation of a test portion begins with clause 6.4.

b) In 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

a) The user shall provide objective evidence of the performance of the method as implemented in their facility. This is necessary to enable the user and their customers to understand the limitations of the method and to make decisions using the results of analyses. Critical aspects of method performance are

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Preferred Line</th>
<th>Secondary Line</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium, Cd</td>
<td>K-L₂,₃ (Ka)</td>
<td></td>
</tr>
<tr>
<td>Lead, Pb</td>
<td>L₂-M₄₅ (Lβ₁)</td>
<td>L₃-M₄₅ (Lα₁,₂)</td>
</tr>
<tr>
<td>Mercury, Hg</td>
<td>L₃-M₄₅ (Lα₁,₂)</td>
<td></td>
</tr>
<tr>
<td>Chromium, Cr</td>
<td>K-L₂,₃ (Ka)</td>
<td></td>
</tr>
<tr>
<td>Bromine, Br</td>
<td>K-L₂,₃ (Ka)</td>
<td>K-M₂,₃ (Kβ₁,₂)</td>
</tr>
</tbody>
</table>

Given the variety of spectrometers and associated software operating systems, it is acceptable for the user 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 at the time of method implementation. Evidence of maintenance of performance may be obtained through the use of control charts or by repeating the measurements and calculations made at implementation.
b) Spectrometer sensitivity is used as a figure of merit to compare spectrometers and 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 purpose of discussion, the correction of line overlaps is considered as part of the spectrometer calibration.

d) The Limit of Detection, $L_D$, shall be estimated at 95% confidence level for each set of operating conditions employed in the test method using Equation 1 below, accepted in analytical atomic spectrometry.

$$L_D \approx 3\sigma$$

where $L_D$ is expressed in units of concentration and $\sigma$ 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 estimate of standard deviation, $\sigma$) is substituted for $\sigma$.

**NOTE**: Detection limit 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. Detection limit 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 detection limits may also change. For optimum performance, the detection limit shall 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 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 is in statistical control. If destructive sample preparation precedes the measurement, the repeatability should be tested inclusive of sample preparation, otherwise, repeatability of the measurement should be tested on the same sample. Repeatability is expressed as the standard deviation of at least seven (7) 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 (5) times the detection limit estimated in 6.5.4 d).

### 6.5.5 Tests

a) Position the test portion in the correct position for measurement with the XRF spectrometer.

b) If necessary, establish the required atmosphere in the chamber of the spectrometer and allow it to stabilize.

**NOTE**: Typically, the measurements are made in an air atmosphere. However, should there be a need to measure light elements such as sulphur, aluminium, etc., it may be advantageous to measure in a vacuum or helium atmosphere.

c) Measure the test portion by collecting sufficient numbers of X-ray counts to attain counting statistical uncertainty less than the established relative standard deviation for measurement repeatability. (See 6.5.4 f))

### 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 can be found in the annex to this clause.

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 analyzed

- Empirical (traditional) calibration using a model based on influence coefficients obtained
  — using empirical data from a suite of calibration standards similar to the unknowns or
  — using a fundamental parameters approach.

Follow the guidelines in the instrument’s users 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 analyzed. In the set of calibrants, element concentrations shall cover the range of concentration expected in the specimens and they shall vary independently of one another. If the calibration covers many elements in a wide range of concentrations, a high 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

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 parameters shall be specified in the work instructions for the test method. Calculate the result for each analyte, in % 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.

c) 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.

— The preferred method is to create an uncertainty budget for each calibration implemented in the test method. The uncertainty budget shall be compliant with the Guide to the Expression of Uncertainty in Measurement published by the International Organization for Standardization (ISO). Express the expanded uncertainty estimate at the 95 % confidence level.

NOTE: 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, the potential for introduction of bias during sample preparation, and more. Definition of an uncertainty budget is beyond the scope of this standard.

— This method recognizes that it may be impractical or impossible to perform proper uncertainty budget. Therefore, as an alternative to 6.6 c), choose a safety factor greater than or equal to the expected expanded uncertainty for each analyte at the level of the maximum allowed concentration. Experts consulted during the development of this test method agreed 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 equal for the purpose of making decisions regarding the need for additional testing.

NOTE: The use of a safety factor is an oversimplification due in part to the fact that in most cases relative uncertainty is a function of concentration. Typically, relative uncertainty increases rapidly as 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 Precision

Method precision, i.e. repeatability and reproducibility, are to been determined through an interlaboratory test. Examples of method performance are described below.

6.8 Quality Assurance and Control

6.8.1 Accuracy of calibration

a) The accuracy of each calibration shall be validated by analyzing one or more reference materials representative of each material within the scope of each calibration 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, there will be reference materials available to bracket the maximum allowed values.

b) Results of measurements of the reference materials shall be calculated and expressed according to clause 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 National Institute of Standards and Technology Special Publication 829 or similar documents.

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

6.8.2 Control samples

a) Designate a quantity of stable material as the control sample for each calibration. Preferably, this should be a solid in form of a 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 (4) 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 of a new control sample.

6.9 Special Cases

6.9.1 Presentation of Sample for Measurement

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

b) If the measurement is performed with a portable, hand-held XRF analyzer care shall be taken to ensure that the analyzer measuring aperture covers the section to be analyzed.
c) Analysis of specimens which are not flat or large enough to cover measuring aperture of 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, the analyst shall carefully position one or more of the items in the proper holder prior to measurements following manufacturer’s recommendations, and obtain an estimate of the composition using the software tools provided by the method.

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

6.9.2 Uniformity of the Sample

The uniformity from the point of view of XRF analysis depends on physical uniformity of the composition of tested material within the volume of material irradiated by 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 tested material, for purposes of XRF analysis, is made visually and with help of any additional information available. For example, any object that appears uniform in color, 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 tapes, metal alloys, etc. Any additional information about tested object should be used to establish its uniformity. For example, many plastic and even more so metal enclosures are painted. Plastic enclosures may be metallized, often on the inside. In such cases the test should be performed on unpainted or 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, cadmium on steel, chromium on steel and aluminum. These will be indicated by relatively very high readings of plating metals, with possible exception of Cr whose coatings are typically very thin. All coatings should be removed, when attempting to analyze the base material.

b) Small area samples:
   - Small electronic parts may also be treated as uniform as long as the instrument used for analysis can irradiate and analyze only selected segments of small electronic components. The sample should appear uniform, such as plastic encapsulation, individual soldering lead, or isolated area of polymer/epoxy. Special care should be taken to avoid the complications of metal plating, polymer coating, or paint interferences, when analyzing the base material. The coatings should be physically removed, if present.

c) Coatings and thin samples:
   - Specimens that are too small or very thin may easily violate the condition of minimum sample thickness or mass that shall be present in order for the results to be valid. In such instances a number of small objects of the same kind (for example small screws) should be placed in a sample cup and then only analyzed. Similarly, thin samples of the same kind should be stacked in the pile thick enough to fulfill the minimum sample thickness criterion and analyzed accordingly. As a general rule, all samples shall completely cover the measuring window/area of the spectrometer. The sample should be at least 5 mm thick in case of polymers and light alloys such as Al, Mg or Ti, minimum of 15 mm thick in case of liquids and about 1 mm thick for all other alloys. The insulation on thin wires and ribbon cables may not be treated as uniform and should be measured by extracting the metal conductor first. On the other hand, almost all power cords of 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 analyzed, after separation. Some metal coatings may be analyzed, if the user knows the construction of the material, and the spectrometer is calibrated to analyze such a complex layer system. For example, the coatings is known to be SnAgCu (plated over) Copper (plated over) epoxy. The tin alloy may be analyzed, 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 nm in thickness. Due to variations from instrument to instrument of the required sample size, the operator of the spectrometer is advised to always consult the instrument manual or manufacturer for requirements on minimum size/mass/thickness conditions of the sample.

d) The numerical screening limits listed (Table 4) may not be appropriate to determine regulatory compliance of all possible samples, particularly if the sample is a composite of different product materials. This especially might 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 speaks of uniformity for the sake of accurate XRF analysis and does not attempt to make a “legal” determination about sampling requirements.

e) Summary:

The tested object may be considered as uniform and analyzed nondestructively if:

— it is not painted or plated and appears to the eye as of the same color 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 analyzed, separately from the base material in a known matrix only, and the instrument is calibrated for this know matrix.

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

6.10 Annex (Informative): Practical Application of Method

The following clauses provide 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 document, assures the operator of the best possible quality of analytical results.

6.10.1 Matrix and Interference Effects

As general guidance, 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 for 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 take place:

b) Absorption of excitation radiation and fluorescence radiation by the analyte and by the other elements (matrix) in the sample.

c) Secondary excitation (enhancement) of the analyte by other elements in the sample:

— Plastic materials: In plastics 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 like Ca, Ti, Zn, Sn,… and by such elements as Br and Sb, which originate in flame retardants
  — the secondary excitation by elements like 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 should always be used in this case.
— Metals: In metals 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 table 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, ...
— Electronic components and printed wiring boards: In principle all effects, which are described for polymers and metals.

d) In addition, the intensity of characteristic radiation of the element in the sample can be influenced by interfering line from other elements in the sample. For the elements of interest typically these can 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 in case that the samples contain Ca and Fe in high concentrations
— Cr: Interferences possible from Cl
— Br: Interferences possible from Fe and Pb

e) Influence of matrix effects on LOD

Table 3: Effect of matrix composition on Limits of Detection of some controlled elements

<table>
<thead>
<tr>
<th>Element/Analyte</th>
<th>Pure Polymer</th>
<th>Polymer with ≥ 2 % Sb, no Br</th>
<th>Polymer with ≥ 2 % Br, no Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>A</td>
<td>~ A ▶ 2A</td>
<td>≥ 2A</td>
</tr>
<tr>
<td>Lead</td>
<td>B</td>
<td>~ 2B</td>
<td>≥ 3B</td>
</tr>
</tbody>
</table>

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 the A and B, as in Table 3 above.

NOTE 2: The information in Table 3 above is provided as the guidance only; the actual LODs for the analytes of interest are specific for each instrument and analytical conditions/parameters employed.

6.10.2 Interpretation of Results

For each analyte, the analyst shall prepare an uncertainty budget with an estimate of the overall 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 Eq. 1, the result for the sample is “BELOW LIMIT”.

\[
P_i = L_i - U_i
\]

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 Eq. 2, the result for the sample is “OVER LIMIT”.

\[
F_i = L_i + U_i
\]

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", 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 \( L \) above 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 chemical compound of interest.

− 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 the ISO Guide to the Expression of Uncertainty in Measurement.

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 found in Table 4.

### Table 4: Screening limits in mg/kg for regulated elements in various matrices

<table>
<thead>
<tr>
<th>Element</th>
<th>Polymers</th>
<th>Metals</th>
<th>Composite Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>( BL \leq (70-3\sigma) &lt; X &lt; (130+3\sigma) \leq \text{OL} )</td>
<td>( BL \leq (70-3\sigma) &lt; X &lt; (130+3\sigma) \leq \text{OL} )</td>
<td>LOD &lt; X &lt; (150+3\sigma) ≤ OL</td>
</tr>
<tr>
<td>Pb</td>
<td>( BL \leq (700-3\sigma) &lt; X &lt; (1300+3\sigma) \leq \text{OL} )</td>
<td>( BL \leq (700-3\sigma) &lt; X &lt; (1300+3\sigma) \leq \text{OL} )</td>
<td>( BL \leq (500-3\sigma) &lt; X &lt; (1500+3\sigma) \leq \text{OL} )</td>
</tr>
<tr>
<td>Hg</td>
<td>( BL \leq (700-3\sigma) &lt; X &lt; (1300+3\sigma) \leq \text{OL} )</td>
<td>( BL \leq (700-3\sigma) &lt; X &lt; (1300+3\sigma) \leq \text{OL} )</td>
<td>( BL \leq (500-3\sigma) &lt; X &lt; (1500+3\sigma) \leq \text{OL} )</td>
</tr>
<tr>
<td>Br</td>
<td>( BL \leq (300-3\sigma) &lt; X )</td>
<td>( BL \leq (700-3\sigma) &lt; X )</td>
<td>( BL \leq (250-3\sigma) &lt; X )</td>
</tr>
<tr>
<td>Cr</td>
<td>( BL \leq (700-3\sigma) &lt; X )</td>
<td>( BL \leq (700-3\sigma) &lt; X )</td>
<td>( BL \leq (500-3\sigma) &lt; X )</td>
</tr>
</tbody>
</table>

− A common set of limits for the substances of interest have been assumed for the purposes of this example. The limits are 100mg/kg for Cd and 1000 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 1000 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 for this approach to estimating uncertainty (translated here as “margin of safety”) can be found in clause 6.6c).

− The symbol “X” marks the region, where further investigation is necessary.

− The term “3\( \sigma \)” expresses the repeatability of the analyzer at the action level, where \( \sigma \) is determined as the standard deviation of a typical sample with content of the regulated substances near the limits of interest (see spectrometer performance verification test 6.8.4.6). The repeatability is expresses in terms of “3\( \sigma \)” 99.7 % confidence level rather than the more common “2\( \sigma \)” 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 shall be below the “action level” and should be applied in accordance with the note in clause 6.5.4 d).
### 7 Determination of PBB and PBDE in Polymers by GC-MS

This document describes the procedure for the determination of mono- to decabrominated biphenyl (PBB) and of mono- to nonabrominated diphenyl ether (PBDE) in polymers of electrotechnical products.

**NOTE 1:** For informative purposes the procedure has been developed to also allow detecting and quantifying DecaBDE. It is however important to remind that DecaBDE is not regulated.

The test procedures describe in this clause are intended to be provide the highest level of accuracy and precision for concentrations of the regulated substances that range between 100 mg/kg and 1000 mg/kg.

**NOTE 2:** Higher levels can be similarly evaluated if brought within the range of calibration by dilution of the final extract. The dilution must be factored into the quantitative calculation.

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

#### 7.1 Apparatus / Equipment and Materials

**7.1.1 Apparatus**

- **a)** Analytical balance, accuracy 0.1 mg
- **b)** 1 mL, 5mL, 10 mL, 100 mL measuring flask
- **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 (deactivated at 450 °C)
- **f)** Heating jackets
- **g)** Funnel
- **h)** Aluminium foil
- **i)** Cork rings
- **j)** Microlitre syringe or automatic pipette
- **k)** Pasteur pipette
- **l)** 1.5 mL sample vials with 100 µL glass inset and a screw cap with teflon gasket or, depending on the analytical system, a comparable sample receptacle
- **m)** Minishaker (also known as vortexer or vortex mixer)

**7.1.2 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 800 m/z. The use of an autosampler is strongly recommended for reproducibility.

A column length of approx. 15 m exhibits sufficient separation efficiency for PBB and PBDE compounds.
7.1.3 Reagents

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

a) Toluene (GC grade or higher)
b) Propanol (GC grade or higher)
c) 5/25 Dichloromethane/cyclohexane (B.P. 40 C/81 C) (GC grade or higher)
d) Helium (purity minimum 5.0)
e) PBB & PBDE calibration standards (see 1.8 PBB & PBDE Calibration Standards)
f) Surrogate & internal standards

- Surrogate standard used to monitor analyte recovery according to clause 7.3.1, 7.3.4, 7.4.1, 7.4.2 and 7.6, e.g. DBOFB (4,4'-dibromoctafluorobiphenyl) (n) or C13 labelled Penta or OctaBDE standard

- Internal standard used to correct for injection errors, according to clause 7.3.1, 7.3.5, 7.4.2, and 7.6 e.g. CB209 (2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl)

NOTE: These substances may also be replaced by other suitable standard substances.

7.2 General instructions on the analysis

a) In order to reduce blank values all glass devices and the glass wool should be deactivated at 450 °C. In order to avoid decomposition (debromination) of PBDEs by UV light during extraction and analysis, glass devices made from brown glass should be used if possible. If no brown glass is available, aluminium foil can be used for protection from light.
b) In order to determine the concentrations of all standard solutions and sample extracts, differential weighing is carried out and converted with the help of the density of toluene (0.87 g/mL) or of another solvent used.

7.3 Sample preparation

The samples are ground to a size of 500 µm before the extraction, as described in clause 5.5.6.

7.3.1 Stock solutions

a) Surrogate standard (to monitor analyte recovery): 50 µg/mL in toluene (e.g. DBOFB)
b) Internal standard (to correct for injection error): 0.2 µg/mL in toluene; 1 µg/mL in toluene (e.g. CB209)
c) PBB spiking solution: 50 µg/mL in an organic solvent
d) Polybrominated diphenyl ether (PBDE): 50 µg/mL in an organic solvent

7.3.2 Pre-extraction of the Soxhlet extractors

To clean the Soxhlet extractors, a two-hour pre-extraction is carried out with 70 mL of the appropriate solvent (see clause 7.3.3). The washing solvent is discarded.

7.3.3 Sample extraction

a) Quantitatively transfer approx. 100 mg +/- 10 mg of the sample into the extraction thimbles. Record the weight to the nearest 0.1 mg.
b) Depending on the type of polymer, different solvents should be used for extracting PBBs and PBDEs from polymers. If the nature of the polymer is unknown, Toluene should be used as universal solvent. For specific polymers the following solvents should be used:

- Toluene for ABS (Acrylonitrile Butadiene Styrene), HIPS (High Impact Polystyrene) and PC/ABS (Polycarbonate / Acrylonitrile Butadiene Styrene)
- Propanol for Polyamides and Polyesters
- 5/25 Dichloromethane/cyclohexane (B.P. 40 C/81 C) for Polyolefins
c) The sample is transferred through a funnel into the extraction thimble. In order to ensure a quantitative transfer, the funnel is rinsed with approx. 10 mL of solvent.

d) 200 µL of the surrogate standard [50 µg/mL] is added (in accordance with clause 7.3.1).

e) In order to prevent the sample from floating, the thimble is closed with glass wool. Approx. 60 mL of solvent is put in the 100 mL round-bottomed flask, the equipment is covered with aluminium foil to exclude light and the sample is extracted for about 2 hours (20 extraction cycles).

f) The extract is put in a weighed 100 mL measuring flask and the round-bottomed flask rinsed with approx. 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 can be neglected in this case in the calculation.

g) The measuring flask is filled up with 100 mL of solvent and weighed. The precise volume of solvent is calculated by the density [according to clause 7.4.3].

For a soluble polymer sample, the alternative extraction procedure may be applied as outlined in clause 7.8.2.

7.3.4 Addition of the internal standard

50 µL of the extract is transferred into the glass insert of the sample vial with a microlitre pipette or an automatic pipette and 50 µL of the internal standard [0.2 µg/mL] is added in accordance with Clause 7.3.1. The sample vials are homogenised before the analysis by shaking or vortexes. Inject 1 µL of the sample solution into the GC/MS, and analyze it under the parameters described in clause 7.5.

7.4 Calibration

A calibration curve shall be established for quantitative analysis. At least five calibration solutions shall be made in equidistant concentration steps. Quantification is made based on the measurement of the peak areas. Linear regression curve fit should be applied with a relative method’s standard deviation (RSD) of less than or equal to 15 % of the linear calibration function. Statistical tests to check for linearity should be used for quality assurance, e.g. Mandel’s adjustment test.

NOTE: If the limiting value of RSD 15% is exceeded, from the point of view of quality assurance, 2nd degree does not guarantee any significantly better adjustment. Only statistical tests like the F-test fulfill these requirements by comparing linear/2nd degree. That means that although the RSD value is exceeded, the calibration is linear.

7.4.1 PBB [1 µg/mL for each congener], PBDE [1 µg/mL for each congener] and surrogate standard [0.2 µg/mL] stock solution

100 µL of each PBB and each PBDE stock solution (50 µg/mL) and 20 µL of the surrogate stock solution (50 µg/mL) is put in a 5 mL measuring flask in accordance with clause 7.3.1 and filled up with solvent up to the mark. The solvent volume is determined by differential weighing with the help of the density of the selected solvent.

7.4.2 Calibration

For the external 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] (clause 7.4.1) and the stock solution of the internal standard [1 µg/mL] (clause 7.3.1).

The volumes indicated in Table 5 are put into a 1 mL measuring flask by a pipette and filled up with solvent up to the mark.

NOTE: For DecaBDE, the calibration range suggested in Table 5 may have to be modified. When establishing a calibrating curve for DecaBDE the lower range should be set according to the instruments sensitivity. A higher concentration may be used for the upper range to account for the generally high levels of DecaBDE normally found in samples.
<table>
<thead>
<tr>
<th>No.</th>
<th>Volume PBB+PBDE+ surrogate&lt;sup&gt;1&lt;/sup&gt; [µL] (Clause 1.4.1)</th>
<th>Volume internal standard&lt;sup&gt;2&lt;/sup&gt; [µL] (Clause 1.3.1)</th>
<th>c(PBB) [ng/mL per congener]</th>
<th>c(surrogate) [ng/mL]</th>
<th>c(internal standard) [ng/mL]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>100</td>
<td>50</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>150</td>
<td>100</td>
<td>150</td>
<td>30</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>250</td>
<td>100</td>
<td>250</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>350</td>
<td>100</td>
<td>350</td>
<td>70</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>450</td>
<td>100</td>
<td>450</td>
<td>90</td>
<td>100</td>
</tr>
</tbody>
</table>

<sup>1</sup> surrogate standard to monitor the analyte recovery rate

<sup>2</sup> Internal standard to correct for injection error

The internal standard is used for the correction of the injection error. Therefore the evaluation of the response is carried out by \( \frac{A}{A_{\text{internal standard}}} \)

To produce the calibration straight lines the response \( \frac{A}{A_{\text{internal standard}}} \) is plotted against the concentration \( \frac{C}{C_{\text{internal standard}}} \)

A linear regression is carried out using the equation \( \frac{A}{A_{\text{internal standard}}} = a \times \frac{C}{C_{\text{internal standard}}} + b \)

With:

- \( A \): PBB, PBDE or surrogate peak area
- \( A_{\text{internal standard}} \): internal standard peak area
- \( C \): PBB, PBDE or surrogate concentration per congener in the calibration [ng/mL]
- \( C_{\text{internal standard}} \): internal standard concentration in the calibration [ng/mL]
- \( a \): slope
- \( b \): axis intercept

NOTE: 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.

### 7.4.3 Calculation of PBB and PBDE concentration

The concentrations of PBBs and PBDEs in the samples [mg/g] will be calculated by the following formula:
\[
C \text{ [mg/g]} = \frac{\left( \frac{A}{A_{\text{internal standard}}} - b \right) \cdot c_{\text{internal standard}}}{a} \cdot G \cdot D \text{[mL]} \cdot F \cdot E \text{[g]}
\]

A: PBB, PBDE or surrogate peak area

\(A_{\text{internal standard}}\): internal standard peak area

\(c_{\text{internal standard}}\): internal standard concentration in the calibration [ng/mL]

D: volume of organic solvent [mL]

NOTE 1: If the volumetric (graduated) flasks (according to clause 7.1.1.b) will be deactivated at 450 °C as recommended, accuracy may be lost. It is recommended to calculate D from the weighed amount of extract [g] and the density of solvent according to the formula:

\[
D \text{ [mL]} = \frac{T \text{[g]} \cdot \rho^{-1} \left[ \frac{g}{mL} \right]^{-1}}{}
\]

F: conversion factor of the units (from ng to mg) = 1 x 10^6

E [g]: weighed portion (of polymer)

G: dilution factor (Clause 1.3.5) = 2

T [g]: mass of extract

a: slope

b: axis intercept

\(\rho^{-1}\): Density of solvent

NOTE 2: Additional note based on the experience of the interlaboratory comparison: When calculating the PBDE concentrations in the sample, a potential blank value (according to clause 7.6.1 a)) must be taken into account.

NOTE 3: The calculation shown above is for linear regression calibration only. A separate calculation is required if polynomial regression calibration is utilized.

7.5 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

b) Both PTV or split/splitless injector or comparable injections systems can be used. Following parameters are recommended/optional:
   - PTV programme: 50 °C – 90 °C (0 min) – 300 °C/min – 350 °C (15 min); modus: splitless purge time 1 min; purge flow 50 ml/min;

NOTE: Initial temperature needs to be adjusted by the operator depending on the boiling point of the solvent used.
— 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)
d) Carrier: He, 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) Ionisation method: Electron Ionization (EI), 70 eV

The analysis of PBBs and PBDEs is carried out in SIM (Selected Ion Monitoring) Modus with the mass traces (the underlined mass traces have been used for quantification) given in Table 6 and 7. These have been found suitable and are provided as examples.

**Table 6: Reference masses for the quantification of PBBs**

<table>
<thead>
<tr>
<th>Ions monitored in the extract</th>
<th>Mono-BB</th>
<th>Di-BB</th>
<th>Tri-BB</th>
</tr>
</thead>
<tbody>
<tr>
<td>231.9</td>
<td>233.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>309.8</td>
<td>311.8</td>
<td>313.8</td>
<td></td>
</tr>
<tr>
<td>387.8</td>
<td>389.8</td>
<td>391.8</td>
<td></td>
</tr>
<tr>
<td>307.8</td>
<td>309.8</td>
<td>467.7</td>
<td></td>
</tr>
<tr>
<td>385.7</td>
<td>387.7</td>
<td>545.6</td>
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<td>465.6</td>
<td>467.6</td>
<td>627.5</td>
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<tr>
<td>543.6</td>
<td>545.6</td>
<td>705.4</td>
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<td>623.5</td>
<td>625.5</td>
<td>627.5</td>
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<tr>
<td>701.4</td>
<td>703.4</td>
<td>705.4</td>
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<td>701.4</td>
<td>703.4</td>
<td>705.4</td>
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</tbody>
</table>

( ): Optional ions; Bold: Quantification ions; Underlined: Identification ions.

**Table 7: Reference masses for the quantification of PBDEs**

<table>
<thead>
<tr>
<th>Ions monitored in the extract</th>
<th>Mono-BDE</th>
<th>Di-BDE</th>
<th>Tri-BDE</th>
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</thead>
<tbody>
<tr>
<td>247.9</td>
<td>249.9</td>
<td>249.9</td>
<td>249.9</td>
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<tr>
<td>325.8</td>
<td>327.8</td>
<td>329.8</td>
<td>329.8</td>
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<td>403.8</td>
<td>405.8</td>
<td>407.8</td>
<td>407.8</td>
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<tr>
<td>323.8</td>
<td>325.8</td>
<td>483.7</td>
<td>483.7</td>
</tr>
<tr>
<td>401.7</td>
<td>403.7</td>
<td>561.6</td>
<td>561.6</td>
</tr>
<tr>
<td>481.6</td>
<td>483.6</td>
<td>643.5</td>
<td>643.5</td>
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<tr>
<td>559.6</td>
<td>561.6</td>
<td>721.4</td>
<td>721.4</td>
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<tr>
<td>639.5</td>
<td>641.5</td>
<td>643.5</td>
<td>643.5</td>
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<tr>
<td>717.4</td>
<td>719.4</td>
<td>721.4</td>
<td>721.4</td>
</tr>
<tr>
<td>797.3</td>
<td>799.3</td>
<td>799.3</td>
<td>799.3</td>
</tr>
</tbody>
</table>

( ): Optional ions; Bold: Quantification ions; Underlined: Identification ions.
7.6 Quality Control

a) One reagent blank should be extracted with each sequence of samples. The reagent blank is 60 mL of toluene taken through the entire extraction procedure according to clause 7.3.3 or 7.3.4 but excluding a sample.

b) One sample per sequence or one every ten samples if the sample load dictates, should be spiked with 1 mL of each PBB spiking solution [50 µg/mL of each PBB] and 1 mL of each PBDE spiking solution [50 µg/mL of each PBDE] (reference concentration of recovery should be 250 ng/mL of each PBB and PBDE congener according to clause 7.4.2 referring to the calibration range). Following formula should be used for calculation:

$$ R \% = \left( \frac{c_{\text{spike}} - c_{\text{sample}}}{c_{\text{matrix spike}}} \right) \times 100 \% $$

with $R$: recovery [%] of each PBB or PBDE congener
$c_{\text{matrix spike}}$: concentration of each PBB or PBDE congener in the matrix spike [ng/mL]
$c_{\text{sample}}$: concentration of each PBB or PBDE congener in the original sample [ng/mL]
$c_{\text{spike}}$: Concentration of PBB or PBDE spike solution [ng/mL]

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

c) After every tenth sample run and the end of each sample set, analyze a Continuing Calibration Check Standard (CCC). A CCC is an unextracted mid-range calibration standard (according to clause 7.4.2) that is analyzed as a sample (according to clause 7.3.5 and 7.5). The percent recovery for each congener should be between 70 and 130 %. If the percent recovery for any congener falls outside of this range, the analysis should be repeated. If, after re-analysis, the recovery is still out of range, the analysis is stopped and maintenance should be performed on the system to return it to optimal operating conditions. All samples before the failing CCC may be reported, but all samples after the CCC must be re-analyzed with a new calibration.

d) The surrogate recovery should be monitored for each sample analyzed according to clause 7.3.3 or 7.3.4 and 7.3.5. Acceptable recovery should be between 70 and 130 %. If the surrogate recovery for any sample is outside of these limits, the sample should be re-analyzed. If, after re-analysis, the surrogate recovery is not within these limits, the sample should be re-extracted and re-analyzed.

e) From the results of the five calibration standards (according to clause 7.4.2, Table 5), calculate the average response (peak area) for the internal standard. The internal standard (IS) response for each sample (according to clause 7.3.5) should 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 must be re-analyzed. 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.

7.6.1 Method Detection Limit and Reporting Limit

Annually, a Method Detection Limit (MDL) study must be extracted and analyzed. MDL's are defined as the minimum concentration of a substance that can be measured and reported with 99 % confidence from which a qualitative detection is permissible of a sample 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 Students’ $T$ value for the total number of replicates (n) for n-1 degrees of freedom.

**NOTE 1:** All analyses used to calculate an MDL must 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-681or other).

b) Weigh out 100 mg of the milled polymer and place it in a new extraction thimble. Repeat this step 6 more times.
c) Place extraction thimble in Soxhlet extraction apparatus.

d) Spike the thimble with PBB Spiking Solution (50 µg/mL, 7.1.3) and PBDE Spiking Solution (50 µg/mL, 7.1.3). The mass of each congener spiked should be no greater than 5 µg (reference concentration in the sample extract prior to analysis: 25 ng/mL) except for OctaBDE/BB/nonaBDE/BB congeners and BDE209/BB209 which should be no greater than 10 µg (reference concentration in the sample extract prior to analysis: 50 ng/mL). The range of calibration need to be adjusted to analyse concentrations less or equal to 50 ng/mL, otherwise the results might/will be out of calibration (according to clause 7.4.2).

e) Use the procedure (extraction according to clause 7.3.3 or 7.3.4) to extract each of the samples. Analyze accordingly.

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

g) Each congener should 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, must be repeated for that congener(s).

h) The reporting limit for each congener should be, at a minimum, 3x the respective MDL. Unlike the MDL, which relates to detection only, the reporting limit is a concentration that can accurately be quantitated 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 must also be used for the MDL samples.

7.7 Evaluation of the Method

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

7.8 Annex (Informative)

7.8.1 PBB & PBDE Calibration Standards

All brominated species from mono- to decabrominated biphenyl (PBB) and mono- to decabrominated diphenyl ether (PBDE) are to be included in the calibration. The availability of congener standards for a particular PBB or PBDE (e.g. penta-BDE) may vary from region to region. The following is an example list of commercially available calibration congener that have been found suitable for this analysis.
Table 8: Example list of commercially available calibration congeners that have been found suitable for this analysis

<table>
<thead>
<tr>
<th>PBB</th>
<th>Compound Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>BB-003</td>
<td>4-Bromo biphenyl</td>
</tr>
<tr>
<td>BB-015</td>
<td>4,4'-Dibromo biphenyl</td>
</tr>
<tr>
<td>BB-029</td>
<td>2,4,5-Tribromo biphenyl</td>
</tr>
<tr>
<td>BB-049</td>
<td>2,2',4,5'-Tetrabromo biphenyl</td>
</tr>
<tr>
<td>BB-077</td>
<td>3,3',4,4'-Tetrabromo biphenyl</td>
</tr>
<tr>
<td>BB-103</td>
<td>2,2',4,5',6-Pentabromo biphenyl</td>
</tr>
<tr>
<td>BB-153</td>
<td>2,2',4,4',5,5'-Hexabromo biphenyl</td>
</tr>
<tr>
<td>BB-169</td>
<td>3,3',4,4',5,5'-Hexabromo biphenyl</td>
</tr>
<tr>
<td>Dow FR-250</td>
<td>Technical mixture of nonabromo biphenyl, octabromo biphenyl (80%), and heptabromo biphenyl</td>
</tr>
<tr>
<td>BB-209</td>
<td>Decabromo biphenyl</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PBDE</th>
<th>Compound Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDE-003</td>
<td>4-Bromo diphenyl ether</td>
</tr>
<tr>
<td>BDE-015</td>
<td>4,4'-Dibromo diphenyl ether</td>
</tr>
<tr>
<td>BDE-033</td>
<td>2',3,4-Tribromo diphenyl ether</td>
</tr>
<tr>
<td>BDE-028</td>
<td>2,4,4'-Tribromo diphenyl ether</td>
</tr>
<tr>
<td>BDE-047</td>
<td>2,2',4,4'-Tetrabromo diphenyl ether</td>
</tr>
<tr>
<td>BDE-099</td>
<td>2,2',4,4',5-Pentabromo diphenyl ether</td>
</tr>
<tr>
<td>BDE-100</td>
<td>2,2',4,4',6-Pentabromo diphenyl ether</td>
</tr>
<tr>
<td>BDE-153</td>
<td>2,2',4,4',5,5'-Hexabromo diphenyl ether</td>
</tr>
<tr>
<td>BDE-154</td>
<td>2,2',4,4',5,6'-Hexabromo diphenyl ether</td>
</tr>
<tr>
<td>BDE-183</td>
<td>2,2',3,4,4',5,6-Heptabromo diphenyl ether</td>
</tr>
<tr>
<td>BDE-203</td>
<td>2,2',3,4,4',5,5',6-Octabromo diphenyl ether</td>
</tr>
<tr>
<td>BDE-206</td>
<td>2,2',3,3',4,4',5,5,6-Nonabromo diphenyl ether</td>
</tr>
<tr>
<td>BDE-209</td>
<td>Decabromo diphenyl ether</td>
</tr>
</tbody>
</table>

NOTE: Ballschmiter and Zell classification numbers have been used for PBB and PBDEs.

7.8.2 Alternative Extraction Procedures for Soluble Polymers

For a soluble polymer sample, the alternative extraction procedure may be applied:

a) Take 100 mg of ground sample and measure its weight accurately to 0.1 mg. Other sample amounts may be used for samples with potentially very low or very high PBB and/or PBDE concentrations.

b) Dissolve the sample in a clean beaker with 10 mL of a selected solvent that will dissolve the sample. The solvent volume may also be adjusted accordingly for samples with potentially very low or very high PBB and/or PBDE concentrations.

c) Add 200 µL of the surrogate standard (50 µg/mL) to the solution.

d) Stir the sample until it is completely dissolved or as much as can be dissolved in the solution.

e) Filter the solution through a 0.45 µm filter membrane (or a 0.45 µm PTFE disc with a 5 mL PTFE syringe). Collect the filtrate in a clean, tared 100 mL volumetric flask.
f) Rinse the beaker and remaining residue with three successive portions of solvent used in 7.3.5 2). Filter each rinsate through a 0.45 µm filter membrane (or a 0.45 µm PTFE disc with a 5 mL PTFE syringe). Combine the rinsates in the volumetric flask described in 7.8.1 e).

g) Adjust the solution volume in the flask to 100 mL with the selected solvent. Mix well and measure the final solution weight accurately to 0.1 mg.

h) Follow the analytical procedures described in clauses 7.3.4, 7.4, and 7.5. Calculate the PBB and/or PBDE concentration in the sample according to clause 7.4.3.

i) For a polymer sample that has been completely dissolved in the selected solvent, report the calculated result directly.

7.8.3 Examples of Chromatograms at suggested conditions

The following chromatograms were obtained by using the GC parameters described in 7.5.

Figure 2: Total ion chromatogram of PBDE standards, BDE-1 to BDE-206 (5 µg/ml), BDE-209 (50 µg/ml).
Figure 3: Total ion chromatogram of PBB standards (3.5µg/ml).

Figure 4: Total ion chromatogram of combined PBB and PBDE standards (BDE-1 to BDE-206 5µg/ml, BDE-209 50µg/ml, PBBs 3.5µg/ml).
Table 9: PBB and PBDE congeners in the mix

<table>
<thead>
<tr>
<th>PBB congeners</th>
<th>PBDE congeners</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-2 = 3-Bromobiphenyl</td>
<td>BDE-1 = 2-Bromodiphenyl ether</td>
</tr>
<tr>
<td>B-10 = 2,6-Dibromobiphenyl</td>
<td>BDE-7 = 2,4-Dibromodiphenyl ether</td>
</tr>
<tr>
<td>B-30 = 2,4,6-Tribromobiphenyl</td>
<td>BDE-28 = 2,4,4'-Tribromodiphenyl ether</td>
</tr>
<tr>
<td>B-80 = 3,3',5,5'-Tetrahromobiphenyl</td>
<td>BDE-47 = 2,2',4,4'-Tetrabromodiphenyl ether</td>
</tr>
<tr>
<td>B-103 = 2,2',4,5,6-Pentabromobiphenyl</td>
<td>BDE-99 = 2,2',4,4',5-Pentabromodiphenyl ether</td>
</tr>
<tr>
<td>B-169 = 3,3',4,4',5,5'-Hexabromobiphenyl</td>
<td>BDE-100 = 2,2',4,4',6-Pentabromodiphenyl ether</td>
</tr>
<tr>
<td>B-194 = 2,2',3,3',4,4',5,5'-OctaBB</td>
<td>BDE-154 = 2,2',4,4',5,6'-Hexabromodiphenyl ether</td>
</tr>
<tr>
<td>B-206 = 2,2',3,3',4,4',5,5',6-NonaBB</td>
<td>BDE-183 = 2,2',3,4,4',5,6-Heptabromodiphenyl ether</td>
</tr>
<tr>
<td>B-209 = Decabromobiphenyl</td>
<td>BDE-203 = 2,2',3,4,4',5,5',6-Octabromodiphenyl ether</td>
</tr>
<tr>
<td></td>
<td>BDE-206 = 2,2',3,3',4,4',5,5',6-Nonabromodiphenyl ether</td>
</tr>
<tr>
<td></td>
<td>BDE-209 = Decabromodiphenyl ether</td>
</tr>
</tbody>
</table>
8 Test for the Presence of Hexavalent Chromium (Cr VI) in Colorless and Colored Chromate Coating on Metals

8.1 Scope, Application and Summary of Method

This method provides procedures for the determination of the presence of hexavalent chromium in colorless and colored chromate coatings on metallic samples. Hexavalent chromium 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 hexavalent chromium in a chromate coating layer can change drastically with time and storage conditions. Therefore, this method takes a practical and effective approach to qualitatively detect the presence of Cr(VI) in the coating layer. The samples to be tested should 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: humidity 45-75 RH (relative humidity), temperature 15-35 ºC.

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 an analyst is not certain about the result from a spot-test, or there is a color interference from the background, the boiling-water-extraction procedure shall be conducted for verification. Color interference can often be found in colored chromate coatings and result in false test results. When the presence of hexavalent chromium in a sample is detected using this method, the sample is considered to have a hexavalent chromium coating.

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

8.2 Apparatus / Equipment and Materials

a) Calibrated balance: Analytical balance with accuracy of 0.1 mg.

b) Thermometer, thermistor or other temperature measurement device: capable of measuring up to 100 ºC.

c) Colorimetric equipment: 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 reusable glassware (glass, quartz, polyethylene, Teflon, etc.) including the sample containers should be soaked overnight in laboratory grade detergent and water, rinsed with water, and soaked for four hours in a mixture of dilute nitric and hydrochloric acid (nitric acid: hydrochloric acid: H₂O, 1:2:9 by volume) followed by rinsing with DI water. Alternative cleaning procedures are permitted, provided that 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: a suitable 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 cellulosic or polycarbonate membranes.

8.3 Reagents

a) 1,5-diphenylcarbazide, analytical reagent grade.
b) 1 mg/kg $K_2Cr_2O_7$ standard solution: dissolve 0.113 g $K_2Cr_2O_7$, analytical reagent grade, in DI water and dilute it with DI water in a glass container to total weight of 100 g. The shelf life of this solution is about 1 year. Measure 0.25 g of this solution in a second glass container and dilute it with DI water to total weight of 100 g.

c) Acetone, analytical reagent grade.

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

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

f) Nitric acid: concentrated $HNO_3$, analytical reagent grade or spectrograde quality. Store at 20-25 ºC in the dark. Do not use concentrated $HNO_3$ if it has a yellow tinge; this is indicative of photoreduction of $NO_3^-$ to $NO_2$, a reducing agent for Cr(VI).

g) Hydrochloric acid: 35.5-38 % (m/m), analytical reagent grade or spectrograde quality.

h) DI water, DI water shall be free of interferences.

8.4 Sample Preparation

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

If there is a polymer coating on the top of a sample surface, a gentle abrasion with a fine sandpaper, such as a SiC grinding paper with 800 grit size, may be applied to remove the polymer layer, but without removing the chromate coatings on the sample. Other coating removal methods may be applied if they are proven to be more effective.

8.5 Test Procedures

8.5.1 Spot-test Procedure

a) Dissolve 0.4g of 1,5-diphenylcarbazide in a mixture of 20 mL acetone and 20 mL ethanol (96 % (v/v)). After dissolution, add 20 mL of 75 % (m/m) orthophosphoric acid solution and 20 mL of DI water. Prepare this solution not more than 8 hours prior to use.

b) For a metal plate sample, place 1 to 5 drops of test solution (prepared in procedure a)) on the sample surface. If hexavalent chromium is present, a red to violet color will appear within a few minutes. Ignore any color that appears much later, for example on drying. For a fastener sample, e.g. a small screw, place the sample into a small container, such as a test tube, add 1 to 5 drops of test solution (prepared in procedure a)) into the container. If hexavalent chromium is present, a red to violet color will appear within a few minutes. It is easier to observe the color 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 for the sample, the sample is considered to have a hexavalent chromium coating. 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 metal plate sample surface, or choose another fastener sample of the same kind, apply a gentle rub with a fine sandpaper, such as a SiC grinding paper with 800 grit size, to scratch the possibly reduced chromate surface, but without completely removing the whole chromate coating layer.

— On the newly scratched surface, repeat test procedure b) described above. If the test result is positive, the sample is considered to have a hexavalent chromium coating.

— If the test result is negative again, repeat the first step of d) with more force to scratch deeper into the coating layer, and repeat the second step of d). If the test results remain negative upon reaching the substrate, the sample is considered below the detection limit of hexavalent chromium at the time of testing.
If the color developed during the test is difficult for the analyst to judge, place 1 drop of K₂Cr₂O₇ standard solution (1 mg/kg concentration, prepared in 8.3 b)) on a newly polished bare substrate, and mix it with 1 drop of test solution (prepared in procedure 8.5.1 a)). Or mix equal amount of K₂Cr₂O₇ standard solution (1 mg/kg concentration, prepared in 8.3 b)) and test solution (prepared in procedure 8.5.1 a)) in a small container, such as a test tube. Compare the color obtained from the sample with the color obtained from the K₂Cr₂O₇ standard solution. If the color obtained from sample is the same, or redder than the color from the standard solution, the spot-test result for the sample is positive. If the color obtained from the sample is clear, the test result is negative. If the color obtained from the sample is less red than the color from the standard solution but not clear, go to clause 8.5.2.

A positive spot-test result indicates the presence of Cr(VI) coating. The detected Cr(VI) concentration 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 should not be used as a detection limit (or 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 sandpaper, or a file, or stripping the coating layer with acid solutions.

f) Whenever the analyst is not certain about the spot-test result obtained, the following boiling-water-extraction procedure shall be used to verify the result.

8.5.2 Boiling-water-extraction procedure

a) The test solution prepared in (8.5.1.a)) can be used directly in this procedure. An alternative test solution with much longer shelf life can also be used in this procedure: dissolve 0.5 g of diphenylcarbazide in 50 mL of acetone; dilute slowly, while stirring, with 50 mL of DI water (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 discolored.

b) The sample to be tested shall have a surface area of (50±5) cm². For small parts, such as fasteners, or samples with irregular surface shapes, use a suitable number of samples to get the total required surface area of (50±5) cm².

c) Heat 50 mL of DI water in a suitable beaker (with volume graduation) to boiling and totally immerse the sample(s) inside the beaker. Cover the beaker with a watch glasses. Leach for exactly 10 minutes while the water continues to boil. Remove the sample(s), and cool the beaker and its contents to room temperature. Fill with DI water back to 50 mL if some water evaporated. If the solution is milky or has a precipitate, filter it through a membrane filter (0.45 µm pore size) into a dry beaker. Add 1 mL of orthophosphoric acid solution (8.3 e)) and mix well. Pour half the solution into another dry beaker. Add 1 mL test solution (8.5.1 a), or 8.5.2.a)) to one of the two beakers, mix and observe the color against the other beaker which serves as the blank. A red color indicates the presence of Cr(VI).

d) If the color developed during the test is difficult for the analyst to judge, transfer a portion of the solution to a 1 cm absorption cell. After a reaction time of 2 minutes, measure the absorbance at 540 nm against the blank with a colorimetric equipment.

e) Dilute 1 mL of 1 mg/kg K₂Cr₂O₇ standard solution (8.3 b)) to 50 mL with DI water. Add 1 mL of orthophosphoric acid solution (8.3 e)) and mix well. Add 2 mL test solution (8.5.1 a), or 8.5.2.a)), mix and measure the absorbance as above.

f) If the absorbance value obtained in 8.5.2 d) is equal to, or greater than that obtained in 8.5.2 e), the sample is considered to have a hexavalent chromium coating. If not, the test result is negative.

g) A positive boiling-water-extraction test result indicates the presence of Cr(VI) coating. The detected Cr(VI) concentration in the boiling-water-extraction solution is equal to or greater than 0.02 mg/kg with 50 cm² sample surface area used. However, it shall not be
interpreted as the Cr(VI) concentration in the coating layer of the sample and should not be used as a detection limit (or method detection limit) for this qualitative test.

8.6 Evaluation of the Method

The principle of this method was evaluated and supported by two studies organized by IEC TC111 WG3. The studies were focused on detecting the presence of Cr(VI) in metallic samples. There were fourteen international laboratories that participated in the first study, and twelve international laboratories in the second study.
9 Determination of Hexavalent Chromium (Cr VI) by Colorimetric Method in Polymers and Electronics

9.1 Scope, Application and Summary of Method

This method describes the procedures to measure hexavalent chromium, i.e. Cr(VI), quantitatively in samples of polymers, and electronic components. Hexavalent chromium is toxic to human beings. All potential Cr(VI) containing samples and reagents used in the method shall be handled with appropriate precautions.

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

The Cr(VI) concentration in the extract is determined by its reaction in acidic condition 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 colored 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 hexavalent chromium, the samples and extracts should be stored at ambient conditions until analysis. Ambient conditions are defined as: humidity 45-75 RH (relative humidity), temperature 15-35 ºC. Since the stability of Cr(VI) in extracts is not completely understood, the analyses should be carried out as soon as possible after extraction.

If high levels of contaminants such as organics are present in the samples, an ion chromatographic method is recommended after alkaline digestion, i.e. a measured amount of alkaline extract is filtered and injected into the ion chromatograph. Post-column addition of diphenylcarbazide to Cr(VI) containing eluent is followed by detection of the colored complex at 540 nm.

Possible interferences may be caused by reduction of hexavalent chromium, oxidation of trivalent chromium, or color interference in the colorimetric measurement. The interference parameters may include but are not limited to pH, ferrous iron, sulfide, hexavalent molybdenum and mercury salts.

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

9.2 Apparatus / Equipment and Materials

9.2.1 Apparatus / Equipment

a) Vacuum filtration apparatus

b) Heating and stirring device: capable of maintaining the digestion solution at 90-95 ºC with continuous auto stirring capability or equivalent. A Teflon coated magnetic stir bar 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 Teflon shaft and paddle is recommended.

c) Calibrated pH meter: to read pH range 0-14 with an accuracy ± 0.03 pH units.

d) Calibrated balance: an analytical balance with an accuracy of 0.1mg.
e) Thermometer or thermistor or other temperature measurement device: capable of measuring up to 100 °C.

f) Colorimetric equipment: 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 nitrogen cooling: Capable of grinding polymer samples and electronic components.

9.2.2 Materials

a) Labware: all reusable glassware (glass, quartz, polyethylene, Teflon, etc.) including the sample containers should be soaked overnight in laboratory grade detergent and water, rinsed with water, and soaked for four hours in a mixture of dilute nitric and hydrochloric acid (nitric acid: hydrochloric acid: H2O, 1:2:9 by volume) followed by rinsing with DI water. 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, 1000 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 cellulotic or polycarbonate membranes.

9.2.3 Reagents

a) Nitric acid: concentrated HNO3, analytical reagent grade or spectrograde quality. Store at 20-25 °C in the dark. Do not use concentrated HNO3 if it has a yellow tinge; this is indicative of photoreduction of NO3- to NO2, a reducing agent for Cr(VI).

b) Hydrochloric acid: 35.5-38 % (m/m), analytical reagent grade or spectrograde quality.

c) Sodium carbonate: Na2CO3, anhydrous, analytical reagent grade. Store at 20-25 °C in a tightly sealed container.

d) Sodium hydroxide: NaOH, analytical reagent grade. Store at 20-25ºC in a tightly sealed container.

e) Magnesium chloride: MgCl2 (anhydrous), analytical reagent grade. A mass of 400 mg MgCl2 is approximately equivalent to 100 mg Mg2+. Store at 20-25 °C in a tightly sealed container.

f) Phosphate Buffer:
   — K2HPO4: analytical reagent grade.
   — KH2PO4: analytical reagent grade.

f) Phosphate Buffer:
   — 0.5 M K2HPO4 / 0.5 M KH2PO4 buffer at pH 7: Dissolve 87.09 g K2HPO4 and 68.04 g KH2PO4 into 700 mL of DI water. Transfer to a 1 L volumetric flask and dilute to volume.

f) Phosphate Buffer:
   — Lead Chromate: PbCrO4, analytical reagent grade. Store at 20-25 °C in a tightly sealed container.

f) Digestion solution: Dissolve 20.0 ± 0.05 g NaOH and 30.0 ± 0.05 g Na2CO3 in DI water in a 1 L volumetric flask and dilute to the mark. Store the solution in a tightly capped polyethylene bottle at 20-25 °C and prepare fresh monthly. The pH of the digestion solution shall be checked before using. The pH shall be 11.5 or greater, if not, discard.

f) Digestion solution: Dissolve 141.4 mg of dry potassium dichromate, K2Cr2O7 (analytical reagent grade), in DI water and dilute to 1 mL (1 mL = 50 µg Cr).

f) Digestion solution: Dilute 100 mL potassium dichromate stock solution (clause 9.2.3.i)) to 100 mL (1 mL = 5 µg Cr).
k) Sulfuric acid, 10 % (v/v): dilute 10 mL of distilled reagent grade or spectrograde quality sulfuric acid, $\text{H}_2\text{SO}_4$, to 100 mL with DI water.

l) Diphenylcarbazide solution: Dissolve 250 mg 1,5-diphenylcarbazide in 50 mL acetone. Store in a brown bottle. Discard when the solution becomes discolored.

m) Potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, spike solution (1000 mg/L Cr(VI)): Dissolve 2.829 g of dried (105 ºC) $\text{K}_2\text{Cr}_2\text{O}_7$ in DI water in a 1 L volumetric flask and dilute to the mark. Alternatively, a 1000 mg/L Cr(VI) certified primary standard solution can be used. Store at 20-25 ºC in a tightly sealed container for use up to six months.

n) Potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, matrix spike solution (100 mg/L Cr(VI)): Add 10.0 mL of the 1000 mg Cr(VI)/l made from $\text{K}_2\text{Cr}_2\text{O}_7$ spike solution (clause 9.5 m)) to a 100 mL volumetric flask and dilute to volume with reagent water. Mix well.

o) Acetone: analytical reagent grade. Avoid or redistill material that comes in containers with metal or metal-lined caps.

p) DI water, DI water shall be free of interferences.

9.3 Sample Preparation

Samples should 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 capable of passing through a size 500 $\mu$m sieve, e.g. a brass #35 U.S. Standard Sieve.

9.4 Test Procedure

9.4.1 Extraction

a) Take about 5 g of sample and measure its weight accurately to 0.1 mg. Place the sample into a clean suitable digestion vessel. Alternative sample amounts may also be used for samples with potentially very low or very high Cr(VI) concentrations.

b) For matrix recovery test, take another 5 g (or another chosen amount) of sample, and measure its weight with the same accuracy, and place it into another clean suitable digestion vessel. The spike material should be added directly to the sample aliquot at this point (clause 9.2.3 g or 9.2.3 j), and clause 9.4.5).

c) To each sample, add 50±1 mL of digestion solution (clause 9.2.3.h)) measured with a graduated cylinder. Also add approximately 400 mg of $\text{MgCl}_2$ (clause 9.2.3 e)) dissolved in 0.5 mL of 1.0Mol/L phosphate buffer (clause 9.2.3 f)) to each sample. It is optional to add $\text{MgCl}_2$ to the solution if the analytical techniques used can correct for the possible method induced oxidation/reduction of chromium. For polymer samples that appear to “float” on the surface of the digestion solution, 1-2 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.

d) Stir while heating the samples continuously to 90-95 ºC, then maintain the samples at 90-95 ºC for at least 60 minutes with constant stirring.

e) Gradually cool each solution to room temperature with continued agitation. Transfer the contents quantitatively to the filtration apparatus; rinsing the digestion vessel with three successive portions of DI water. Transfer the rinsates to the filtration apparatus. Filter through a 0.45 $\mu$m membrane filter. If the filter becomes clogged using the 0.45 $\mu$m membrane filter, a large pore size filter paper (Whatman GFB or GFF) may be used to prefilter the samples. Rinse the inside of the filter flask and filter pad with DI water and transfer the filtrate and the rinses to a clean 250 mL vessel. Keep the filtered solid on filter membranes for possible use in assessing low Cr(VI) matrix spike recoveries. Store the filtered solid at 4 ± 2 ºC.

f) With constant stirring while monitoring the pH, slowly add concentrated nitric acid solution (clause 9.2.3 a)) to the 250 mL vessel dropwise. Adjust the pH of the solution to 7.5±0.5.
Remove the stirring device and rinse, collecting the rinsate in the beaker. Transfer quantitatively the contents of the vessel to a 100 mL volumetric flask and adjust the sample volume to 100 mL with DI water. Mix well. The sample digestates are now ready to be analyzed.

9.4.2 Color development and measurement

a) Transfer 95 mL of the digestate to be tested to a clean 100 mL vessel. Add 2.0 mL diphenylcarbazide solution and mix. Slowly add H₂SO₄ solution to the vessel and adjust the pH of the solution to 2±0.5. Transfer quantitatively the contents of the vessel to a 100 mL volumetric flask and adjust the sample volume to 100 mL with DI water. Let stand 5 to 10 minutes for full color development.

b) 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) Correct the absorbance reading of the sample by subtracting the absorbance of a blank carried through the color development procedures.

d) From the corrected absorbance, determine the mg/L of Cr(VI) present by reference to the calibration curve.

9.4.3 Preparation of calibration curve

a) To compensate for possible slight losses of chromium during digestion or other operations of the analysis, treat the chromium standards by the same procedure as the sample.

b) Accordingly, pipet a chromium standard solution (clause 9.2.3.j)) in measured volumes into a 10 mL volumetric flask to generate standard concentrations ranging from 0.1 to 5 mg/L Cr(VI) when diluted to the appropriate volume. A calibration curve should be composed of a minimum of a blank and three standards. An alternative concentration range of the calibration curve should be used if the Cr(VI) concentration in the sample solution is outside the original calibration curve, or dilute samples if they are more concentrated than the highest calibration standard.

c) Develop the color of the standards as for the samples.

d) Transfer an appropriate portion of the solution to a 1 cm absorption cell and measure its absorbance at 540 nm with a colorimetric instrument.

e) Correct the absorbance reading of the sample by subtracting the absorbance of a blank carried through the color development procedures.

f) Construct a calibration curve by plotting corrected absorbance values against µg/mL of Cr(VI). Either linear regression or quadratic fitting can be applied to establish a calibration curve. The correlation coefficient (R²) of the curve shall be larger than 0.99, or a new calibration curve should be built.

9.4.4 Calculation of Analytical Results

a) Cr(VI) concentration (mg/kg) in total sample

\[ \text{Cr(VI) concentration (mg/kg)} = \frac{(A\times D\times F)}{S} \]

where:

- \( A \) = Concentration observed in the digest (µg/mL)
- \( D \) = Dilution factor
- \( F \) = Final digest volume (mL)
- \( S \) = Initial sample weight (g)

b) Relative Percent Difference

\[ \text{RPD} = \left\{ \left| \frac{(S-D)}{(S+D)/2} \right| \right\} \times 100 \]

where:

- \( S \) = Initial sample result (µg)
- \( D \) = Duplicate sample result (µg)

c) Spike Recovery

\[ \text{Spike Percent Recovery} = \left\{ \frac{(SSR-SR)}{SA} \right\} \times 100 \]

where:
SSR = Spiked sample result (µg)
SR = Unspiked sample result (µg)
SA = Spike added (µg)

### 9.4.5 Quality Control

A minimum of one blank per sample batch shall be prepared and analyzed to determine if contamination or any memory effects are occurring. Each batch shall contain ≤20 samples.

A laboratory control sample shall be analyzed at a frequency of one per batch, i.e. utilize the matrix spike solution (clause 9.2.3 n)) or solid matrix spiking agent PbCrO$_4$ (clause 9.2.3 g)) to spike into 50 mL of digestion solution (clause 9.2.3 h)). Alternatively, the use of a certified reference material is recommended when available. Recovery should be in the acceptance range of 80% to 120%, or the sample batch should be reanalyzed.

A separately prepared duplicate sample shall be analyzed at a frequency of one per batch. Duplicate samples shall have a Relative Percent Difference of ≤20%.

A soluble or insoluble pre-digestion matrix spike sample shall be analyzed at a frequency of one per batch. The soluble matrix spike sample is spiked with 1.0 mL of the matrix spiking solution (clause 9.2.3 n)) or at twice the sample concentration, whichever is greater. The insoluble matrix spike is prepared by adding 1-2 mg of PbCrO$_4$ (clause 9.2.3 g)) to a sample or at twice the sample concentration, whichever is greater. The matrix spiked sample is then carried through the digestion process and colorimetric measurement procedures. An acceptance range for matrix spike recovery is 75-125%, or the sample batch should be reanalyzed.

Calibration curves should be composed of a minimum of a blank and three standards. Its correlation coefficient should be ≥ 0.99, or a new calibration curve should be built.

Verify calibration with an independently prepared check standard for every batch. The relative percent difference between the original standard and check standard should be ≤ 10%, or a new calibration curve should be built.

### 9.5 Evaluation of the Method

The precision and accuracy of the method, the detection limit of the method, will be updated here once the suitable amounts of data become available from volunteer laboratories chosen by the IEC TC111 WG3.
10 Determination of Mercury in Polymers, Metals and Electronics by CV-AAS, AFS, ICP-OES, and ICP-MS

10.1 Scope, Application and Summary of Method

This document provides the procedure for the determination of Mercury in materials used in electrotechnical equipment. These materials are polymers, metal materials and electronics (printed wiring boards, cold cathode fluorescent lamps, mercury switches etc.). Batteries containing mercury are to be handled as described in the “Standard Analytical Method” of the Battery Industry (Bibliography Reference a)).

The standard describes the use of four methods CV-AAS (Cold Vapor Atomic Absorption Spectrometry), AFS (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 way of analysis can be selected by experts. CV-AAS is the preferred technique based on sensitivity and ease of use.

The analysis by CV-AAS, AFS, ICP-OES and ICP-MS allows the determination of the target element mercury with high precision (uncertainty in the low percentage range) and/or high sensitivity (down to µg/kg level).

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

Finally in the obtained digestion solution the element mercury is determined by CV-AAS, AFS, ICP-OES or ICP-MS. For AFS, ICP-OES, and IPC-MS, the digestion solution may be analyzed straightway. When using CV-AAS, the mercury is reduced to the elemental state before it is analyzed.

The samples for investigation have to be mechanically pre-prepared before the chemical digestion. In order to fulfill minimum requirements for a correct analysis, maximum grain size and minimum amounts of sample are given within the text. It is highly likely that after the digestion methods solid residues are present. It has to be assured 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 mercury. Nevertheless, if the user assures suitability of a simpler approach, the later may be applied. Any deviation from the described procedures has to 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 has to be taken into account

- Many mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Extreme care shall be exercised in the handling of concentrated mercury reagents. Because of the risk of mercury in some laboratory environments, all labware and sample collection tools should be stored in clean mercury free environment.
- All operation prior to instrument analysis shall operate in the fume hood.
- There should be a condenser to avoid the volatility under the condition.
- When using the microwave oven, be strict to operate according to the directory of supplier.
10.2 Apparatus / Equipment and Materials

a) Scale: Precision level of 0.1 mg
b) Heating digester: equipped with vessels, reflux coolers and absorption vessels (for the digestion of metals and electronics)
c) Microwave sample preparation system: equipped with a sample holder and high-pressure PTFE-TFM or PFA-TFM vessels (for the digestion of metal materials containing significant amounts of zirconium, hafnium, titanium, tantalum, niobium or tungsten, and for plastics)
d) Inductively Coupled Plasma Optical Atomic Emission Spectrometer: ICP-OES
e) Cold Vapor Atomic Absorption Spectrometer: CV-AAS
f) Inductively Coupled Plasma Mass Spectrometer: ICP-MS
g) Atomic Fluorescence Spectrometer: AFS
h) Hydrofluoric acid resistant sample holder: Sample holder of which the sample insertion section and torch have been treated for resistance against hydrofluoric acid.
i) Argon gas: Gas with purity of over 99.99 % (v/v)

NOTE: In general, collection and storage of glassware are critical part of the analysis for mercury, independent from the sample type to be analyzed. Because of the sensitivity of the described mercury analytical techniques, each single sampling step should be done with great care. All sampling, storage and manipulation devices have to be mercury-free. Soak all glassware with 50 % (m/m) nitric acid for 24 hours at room temperature, and then rinse thoroughly with grade 1 water, specified in ISO 3696:1987.

j) 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 an alternative to volumetric flasks.
k) Pipettes: such as 1 mL, 2 mL, 5 mL, 10 mL, etc. (PTFE/PFA equipment or glassware).
l) Micropipettes: such as 200 µL, 500 µL, 1000 µL, etc.
m) Glass microfiber filter (borosilicate glass), pore size: 0.45 µm and a suitable filter cup (for microwave digestion)

n) Glass fiber filter 0.45 µm (for wet digestion)
o) Plastic containers for standards and digestion solutions

10.3 Reagents

a) Water: Grade 1 specified in ISO 3696:1987 used for preparation and dilution of all sample solutions
b) Nitric acid (conc. nitric acid): \( \rho(\text{HNO}_3) = 1.4 \text{ g/mL} \), 65 % (m/m), trace metal grade
c) Potassium permanganate: G.R. 5 % aqueous solution (w/v): Dissolve 5 g of potassium permanganate in 100mL of reagent water
d) Fluoroboric acid: HBF\(_4\) 50 % (m/m), trace metal grade
e) Hydrogen peroxide: \( \text{H}_2\text{O}_2 \) (30 % (m/m)), trace metal grade
f) Sodium hydroxide: flakes: NaOH flakes, free of mercury
g) Sodium tetrahydridoborate (sodium borohydride): \( \text{NaBH}_4 \), trace metal grade
h) Potassium borohydride (trace metal grade), sodium hydroxide, G.R. 1 % in 0.05 % NaOH: Add approximately 1000 mL of reagent water to a 1L volumetric flask followed by the addition of 0.05 g sodium hydroxide. Add to 10.0g potassium borohydride and stir to dissolve. Dilute it to scale with reagent water
i) Standard solution with 1000 µg/mL of mercury, trace metal grade
j) Internal standard solution, trace metal grade

— Internal standard elements that do not interfere with the target element will be used for ICP-OES and ICP-MS. Also, the presence of these internal standard elements in the sample solution must be at negligible levels. Sc, In, Tb, Lu, Re, Rh, Bi and Y may be used as internal standard elements.
— For the use with ICP-OES, Sc or Y is recommended, for use with ICP-MS, Rh is recommended. The recommended concentration is 1000 µg/L.

10.3.1 Contaminations

Contaminations can be a major source of error when working in the 1ng range by using the instruments. Cautious handling of apparatus and careful technique will minimize this problem. The following precautions contribute to avoiding sample contamination:

a) Use only Grade 1 water (10.3.a)). Care shall be taken that all materials in contact with the water are free of mercury.

b) Chemicals used for sample preparation can be a major source of contamination. Only reagents that are free of mercury should be used.

c) It is therefore highly recommended to measure the blank values of the reducing agents and the other chemicals before using them for sample preparation.

d) Beakers, pipettes, volumetric flasks, etc., are all major sources of metal contamination. It is essential to use mercury free plastics or quartz glassware for sample handling.

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

10.4 Sample Preparation

10.4.1 Test portion

The different analytical procedures, which can be used alternatively according to this standard, need different amounts of sample in order to achieve the required quality of results.

In the case of electronics, the sample first shall be destroyed mechanically by appropriate means (e.g.: grinding, milling, mill-cutting) before chemical dissolution of the powder can start. In order to assure a representative sample taking at this step, a certain grain size as a function of the starting amount of sample is required (see corresponding clause for mechanical sample preparation).

Cold cathode fluorescent lamps (CCFL) and samples containing liquid mercury are to be frozen and crushed subsequently, before they can be handled as described in this clause. It is recommended to follow here the instructions of California EPA SOP No. 914-S. (Reference b)).

The resulting concentrated solutions may be used directly in AFS, ICP-OES and ICP-MS, i.e. the digestion solution may be analyzed straightway. By using CV-AAS (cold vapor atomic absorption spectrometry) technique, the mercury is reduced to the elemental state before it is analyzed.

10.4.2 Wet Digestion (Digestion of metal materials and electronics)

Wet digestion is recommended for the digestion of metal materials and electronics, exempting metal materials containing significant amounts of silica (Si), zirconium (Zr), hafnium (Hf), titanium (Ti), tantalum (Ta), niobium (Nb) or tungsten (W). For these materials and for plastics, a microwave digestion as described in 10.4.3 is recommended.

a) Approximately 1 g sample is weighed into the reaction vessel and 30 mL conc. HNO₃ (10.3.b)) is added. (In cases where the available sample amount is 500 mg or less, follow the instructions of 10.4.3) The vessel is furnished with a reflux cooler and an absorption vessel (on the top of the reflux cooler; see Figure 5) containing 10 mL 0.5 Mol/L HNO₃, before a temperature program is started to digest the samples for 1h at room temperature and for 2 h at 90 °C. After cooling to room temperature, the content of the absorption tube is put into the reaction vessel and the obtained solution is transferred into a 250 mL
volumetric flask and filled up with 5 % (m/m) HNO₃ to the mark (if the sample is digested completely).

b) For ICP-OES and ICP-MS measurements the obtained sample solution may be diluted with water to the appropriate concentration levels. If an internal standard is to be used, it has to be added before filling up: for a volume of 250 mL, 250 µL of internal standard (10.3 j)) for ICP-OES measurements has to be added, and 250 nL for ICP-MS measurements, respectively.

c) If the sample is not digested completely (e.g. printed wiring boards), the sample is filtered over a 0.45 µm filter and the solid residue is washed four times with 15 mL 5 % (m/m) HNO₃. The obtained solution is transferred into a 250 mL volumetric flask and filled up with 5 % (m/m) HNO₃ to the mark.

d) If there are sample remnants on the filter, they shall be weighed to determine if they represent a significant fraction of the mass of the original sample. If so, they shall be tested for the presence of the analyte.

NOTE: It may be possible to measure the remnants using X-ray fluorescence spectrometry, if the detection limit is sufficiently low.

10.4.3 Microwave digestion

A microwave digestion is recommended for the following materials:

- metals containing significant amounts of silica (Si), zirconium (Zr), hafnium (Hf), titanium (Ti), tantalum (Ta), niobium (Nb) or tungsten (W)
- polymers
- in cases, where the available sample amount is smaller than 0.5 g

NOTE 1: It is highly recommended to weigh in same sample amounts and same type of samples in one digestion run.

NOTE 2: Hg may be determined in the same solution with Pb and Cd obtained by closed system for acid decomposition mentioned as clauses 12 to 14.

a) About 100 mg of the material are weighed into a PTFE-TFM or PFA-TFM vessel. 5 mL of conc. HNO₃, 1.5 mL 50 % (m/v) HBF₄ solution, 1.5 mL 30 % (m/m) H₂O₂ and 1mL water are added. The vessel is closed and the sample is then digested in the microwave oven following a digestion program specified in advance. An example for a suitable microwave program is given in the annex.

b) After cooling the vessel to room temperature (approximately required time: 1 h), it is opened and the solution is filtered over a glass microfiber filter (0.45 µm) into a 25 mL flask, washed and filled to the mark with distilled water.

— If there are sample remnants on the filter, they shall be weighed to determine if they represent a significant fraction of the mass of the original sample. If so, they shall be tested for the presence of the analyte.

NOTE: It may be possible to measure the remnants using X-ray fluorescence spectrometry, if the detection limit is sufficiently low.

10.5 Test Procedure

10.5.1 Standard preparation / Stock solution preparation

These guidelines on standard preparation are general and may need to be modified with respect to the analytical technique and instrumentation used.

a) CV-AAS and ICP-MS:

— Stock solution: Standard mercury solution (10.3.i))

— Standard solution: Take 100 µL of stock solution into a 100 mL volumetric flask; add 1 to 2 drops of potassium permanganate (5 % (m/m) KMnO₄; 10.3.c)) and fill up to the mark with 1.5 % (m/m) HNO₃.

— Aliquots of calibration: 100 µL, 200 µL, 500 µL
Corresponding to: 100 ng, 200 ng, 500 ng Hg

Diluent: 1.5 % (m/m) HNO₃

Calibration volume: 10 mL

Reductant: 3 % (m/m) NaBH₄ in 1 % (m/m) NaOH: Dissolve NaOH flakes (10.3.f)) and NaBH₄ powder (10.3.g)) in water (10.3.a)) and filter

NOTE 1: A reductant solution containing sodium borohydride in sodium hydroxide solution is recommended. In case the available mercury hydride system can not deal with this reductant, tin(II)chloride can be used instead. Thereby the instructions of the Operator's Manual for the instrument should be followed.

Standards should be stored in mercury free plastic containers. The stock solution (10.3.i)) is usually stable for at least a year, whereas standard solutions should be prepared daily.

The stability of mercury standard solutions can be severely affected due to adsorption on the walls of the storage vessel. Therefore it is recommended to stabilize mercury standard solutions by an addition of a few drops of 5 % (m/m) KMnO₄ solution.

b) ICP-OES and AFS:

Standard solution: Take 1 mL of mercury standard solution, see 10.3.i, (corresponding to 1000 µg Hg) into a 100 mL volumetric flask; add 1 - 2 drops of potassium permanganate (5 % (m/v) KMnO₄) and fill up to the mark.

NOTE 2: 1 % (m/v) Au solution can also be used instead of potassium permanganate.

10.5.2 Calibration

a) Check and verify that the instrument can run normally.

b) Under the normal instrument state, set instrument parameter, generate a straight-line regression and confirm that the correlation coefficient (R²) is no less than 0.9995.

c) Calibrate the instrument with a calibration blank and insure that the result of the blank is lower than the method detection limit. If the calibration blank result is higher than MDL, check the instrument and the experiment process until the problem is solved.

d) Calibrate the instrument with three liquid standard solutions prepared from mercury standards; the calibration solutions range shall cover no more than two orders of magnitude. Analyze a check standard. If the analysis results of the check standard still exceed the range ±2 % of the real value, then the instrument is normal; otherwise repeat the analysis. If the analysis results still exceed ±2 % of the real value, check the instrument until the problem is solved.

e) For CV-AAS the standard calibration plot is established as follows:

Using suitable micro liter pipettes, 100 µL, 200 µL and 500 µL of standard solution (corresponding to the weight of 100ng, 200ng and 500ng of mercury) are dispensed into 10mL 1.5 % (m/m) HNO₃, the measurements are done and the calibration plot is set up.

f) The obtained calibration curve shows the relationship between concentrations and absorption of the wavelength for CV-AAS, intensities of atomic spectra lines for ICP-OES, intensities of mass charge ratio for ICP-MS, and intensities of fluorescence for AFS, respectively.

In the case of internal standard method, calibration curve shows the relation between concentrations and the ratio of the reading for Hg and the reading for internal standard element.

10.5.3 Instrument performance

a) After the initial calibration, perform the instrument calibration with quality control materials. If the analysis results exist in the range of ± 2 % of the real value, continue sample analysis; otherwise repeat the analysis. If the analysis results still exceed ±2 % of the real value, terminate the analysis process and check the instrument and experiment process until the problem is solved.
b) During the analysis process, run the method blank with each batch or every ten samples whichever is the greater frequency. The elemental concentration measured in the method blank solution should be less than MDL, otherwise repeat the analysis of the method blank. If the analysis results still be higher than MDL, then stop the analysis process, then recalibrate the instrument and reanalyze the previous ten samples.

c) During the analysis process, run a liquid standard solution with each batch or every ten samples whichever is the greater frequency. If the analysis results exist in the range of ±2% of the real value, then the instrument is normal; otherwise repeat the analysis of the liquid standard solution. If the analysis results still exceed ±2% of the real value, then recalibrate the instrument and reanalyze the previous ten samples.

10.5.4 Sample Analysis

Analyze the method blank, samples solutions and spiked samples solution. Every sample should be determined twice and the relative standard deviation should be no more than 5% and the recovery of spiked samples should be between 95% and 105%.

If the sample solution concentration does not fall within the range of the calibration standards, prepare a serial sample dilution or additional standards to bracket the sample concentration.

NOTE: For CV-AAS measurements the standard or digestion solution is to be transferred into the hydride system beaker. The measurement is conducted using the instrument manufacturer’s instructions. For measurements with ICP-OES, ICP-MS or AFS, the digestion solution can be determined directly.

CV-AAS: 100 µL of the sample solution is given to 10mL 1.5 % (m/m) HNO₃ and the measurement is done.

10.5.5 Calculation of Analytical Results

The concentration measured in 10.5.5 is the concentration of mercury in the sample solution. The concentration of mercury in the sample is calculated from the following equations.

a) ICP-OES

Mercury µg /g = (A₁ – A₂) V / m

where A₁ is the concentration of each target element in the sample solution in mg/L; A₂, the concentration of each target element in the laboratory reagent blank in mg/L; V, the total volume for the sample solution in mL (depends on the particular series of dilutions taken); and m, the measured quantity of the sample in g.

b) AFS and ICP-MS

Mercury µg /g = (A₁ – A₂) V / (1000 m)

where A₁ is the concentration of each target element in the sample solution in µg/L; A₂, the concentration of each target element in the laboratory reagent blank in mg/L; V, the total volume for the sample solution in mL (depends on the particular series of dilutions taken); and m, the measured quantity of the sample in g.

c) CV AAS

Mercury µg /g = V \cdot X / (A \cdot m)

where V is the total volume of the digestion solution in mL (250 mL for wet digestion, 25 mL for microwave digestion); X, the determined weight of metal in sample aliquot in µg; A, the sample aliquot in mL (0.1 mL); and m, the measured quantity of the sample in g (1 g for wet digestion, 0.1 g for microwave digestion).

10.6 Evaluation of the Method

The precision and accuracy of the methods, the detection limits of the methods, and the way how to assure these qualities of data and determination process will be updated here once
the suitable amounts of data become available from volunteer laboratories chosen by IEC TC 111 WG 3.

10.7 Annex (Informative)

Figure 5: Heating digester equipped with reaction vessel, reflux cooler and absorption vessel

Table 10: Program for microwave digestion of samples (power output for five vessels)

<table>
<thead>
<tr>
<th>Step</th>
<th>Time (min)</th>
<th>Power output (W)</th>
<th>Pressure limited to (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>5</td>
<td>400</td>
<td>3.5</td>
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</tr>
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<td>3</td>
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<td>3</td>
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<td>4.0</td>
</tr>
<tr>
<td>Ventilation step</td>
<td>20</td>
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<td>-</td>
</tr>
</tbody>
</table>

10.7.1 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 band width: 0.7 nm
— Purge gas: N₂ or Ar
— Reduction agent: 3 % (m/v) NaBH₄ in 1 % (m/v) NaOH

b) ICP-OES
— Hg wavelength: 194.227 nm
— RF generator power: 1150 W
— Frequency of RF generator: 27.12 MHz
— Argon pressure: 0.16 MPa
— Argon flow Carrier gas: Cool gas: 14 L/min, Auxiliary gas: 0.5 L/min
— Sample uptake rate: 1.6 mL/min

c) ICP-MS
— Mass-charge-ratios for Hg: m/z= 199, 200, 201, 202
— RF generator power: 1200 W
— Frequency of RF generator: 27.12 MHz
— Argon pressure: 0.28 MPa
— Argon flow Carrier gas: Cool 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.

d) AFS
— Source: Hg hollow cathode lamp, Current: 30 mA, Wavelength: 253.7 nm
— Minus high-voltage: 360 V
— Oven temperature: 800 °C
— Argon flow carrier gas: 0.6 L/min, Screen gas: 1.0 L/min
— Reducing regent: Potassium borohydride
— Wash water: 6 % (m/m) HNO₃
11 Determination of Lead and Cadmium in Polymers by ICP-OES, ICP-MS, and AAS

11.1 Scope, Application and Summary of Method

This document specifies the procedure for the determination of elemental lead (Pb) and elemental cadmium (Cd) in polymers from electrotechnical equipment. The document describes the use of three methods (ICP-OES, ICP-MS and AAS) and several procedures for chemical sample preparation, i.e. the sample solution, from which the most appropriate way 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 for ICP-OES and AAS from 10 mg/kg for cadmium and 100 mg/kg for lead and for ICP-MS from 0.1 mg/kg for cadmium and lead. The procedures are not limited for higher concentrations.

The samples are precut and/or milled to an appropriate size for the method selected according to the procedure describe in clause 5. Depending on the particular method for preparing the test solution, sample amounts may vary, as is described in detail in the text. 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 performed in a closed system by use of a microwave digestion vessel. Depending on the presence of particular elements, the detailed approach for digestion varies - procedures are given in the text. Information about the presence of these elements may have been gained from previous screening experiments. Finally in the obtained digestion solution the elements cadmium and lead are simultaneously determined by ICP-OES, ICP-MS or separately by AAS.

The analysis by ICP-OES, ICP-MS or AAS allows the determination of the target elements with high precision (uncertainty in the low percentage range) and/or high sensitivity (down to µg/kg level). There are some limitations: The procedure does not apply for materials containing polyfluorinated polymers because of their stability. If sulfuric acid has to be used within the analytical procedure, there is a risk of loosing Pb, thus resulting in minor values for this analyte. The use of appropriate, sophisticated equipment i.e. microwave digestion system is strongly advised. However, if the experts can assure its suitability, simpler alternatives may be used, e.g. addition of Boric acid instead of using a HF-resistant sample holder. Frequently occurring spectral interferences are given in Table 11.

Limitations and risks occur due to the solution step of the sample, e.g.: precipitation of the target or of other elements may occur; in this case the remnants have to be checked separately or dissolved by another way and then fused with the test sample solution.

The work according to this standard implies the use of toxic and hazardous substances. Detailed warnings are given in the text.

11.2 Apparatus/Equipment and Materials

11.2.1 Apparatus/Equipment
a) ICP-OES: Equipment consisting of sample holder, plasma torch, spray chamber, nebulizer, interface, ion lens, mass separator, optical unit, detector, system control and data output device;
b) ICP-MS: Equipment consisting of sample holder, ionizer, interface, ion lens, mass separator, detector, evacuated vessel, system control and data output device.
c) AAS: Apparatus consisting of a single–slot burner head, hollow cathode lamps, detector, data processor and control system.
d) Hydrofluoric acid resistant sample introduction system: System into where the sample insertion section and torch have been treated for resistance against hydrofluoric acid.
e) Argon gas: Gas with purity of over 99.99 % (v/v)
f) Acetylene gas: Gas with purity of over 99.99 (v/v)
g) Scale: Precision level of 0.1 mg
h) Glassware: All glassware shall be cleaned with 10 % (m/m) nitric acid before use
   - Kjeldhal flask: 100 mL
   - Beakers: such as 100 mL, 200 mL, etc.
   - 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.
   - Pipettes: Such as 1 mL, 5 mL, 10 mL, 20 mL, etc.
   - Funnel
   - Watch glass
   - Crucibles: Such as 50 mL, 150 mL, etc.
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) / Perfluoroalkoxy (PFA)): All
   equipment shall be cleaned with 10 % (m/m) nitric acid before use
   - Beakers: Such as 100 mL, 200 mL, etc.
   - 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 calibration standard
   - Containers made of high-density polyethylene to be used for ordinary measurement of
     element concentration. For determination on the ultratrace level, containers made of
     perfluoroalkoxy (PFA) or fluorinated ethylene-propylene copolymer (FEP). In either
     case, the user shall confirm the suitability of the container selected.

n) Electric hot plate or heated sand bath
o) Muffle furnace: capable of being maintained 450 ± 25 °C temperature.
p) Bunsen burner, or similar type of gas burner.
q) Microwave digestion system
   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.
r) PTFE Microwave digestion vessel: Such as 100mL, etc.
s) Heat resistant thermal insulation board
t) Paper filter

11.3 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 should be
negligible compared to the lowest concentration to be determined.

All reagents for ICP-MS analysis including acids or chemicals in use should be high purity ones: trace metals in total less than 1×10-6 % (m/m).

a) Water: Grade 1 specified in ISO 3696:1987 used for preparation and dilution of all sample
   solutions.
b) Sulfuric acid: ρ(H₂SO₄) = 1.84 g/mL, 95 % (m/m)
c) Nitric acid: ρ(HNO₃) = 1.40 g/mL, 65 % (m/m)
d) Hydrogen-peroxide: ρ (H₂O₂) = 1.10 g/mL, 30 % (m/m)
e) Hydrochloric acid: \(\rho (\text{HCl}) = 1.19 \text{ g/mL}, 37 \% (\text{m/m})\)

f) \(\rho (\text{HF}) = 1.18 \text{ g/mL} (50 \% (\text{m/m}))\)

gh) Boric acid (\(\text{HBO}_3\))

h) Certified Standard solution with 1000 \(\mu\)g/L of lead

i) Certified Standard solution with 1000 \(\mu\)g/L of cadmium

j) Certified Internal standard solution

— Internal standard elements that do not interfere with the target element will be used. 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 the use with ICP-OES, Sc or Y is recommended, for the use with ICP-MS, Rh is recommended. The concentration used should be 1000 \(\mu\)g/L.

NOTE 1: The toxicity of each reagent listed under b) to j) in this method has not been precisely defined; however, each chemical compound needs to be treated as a potential health hazard. From this viewpoint, exposure to these chemicals to 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 spectacles should be worn when handling acids.

NOTE 3: Toxic fumes are evolved by nitric acid. Always carry out digestion in a fume cupboard, as well as addition of 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 precaution measures should be taken in case that hydrofluoric acid is used i.e. HF antidote gel for first aid treatment of HF burns on the skin.

11.4 Sample Preparation

11.4.1 Test portion

The different analytical procedures, which can be used alternatively according to this standard, need different amounts of sample in order to achieve the required quality of results. Generally it is advised to start with the highest amount of sample suitable for the chosen procedure. For further considerations see risks.

For the 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.

11.4.2 Preparation of test solution

11.4.2.1 Dry ashing method

a) When sample does not contain halogen compounds (information may be available from previous screening)

— The sample is measured into a crucible mounted in the hole in the heat resistant thermal insulation board. The crucible is then heated gently with the burner in a hood for proper ventilation, taking care that the sample is not ignited. 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. The crucible and its contents are then transferred to the muffle furnace at 450 ± 25 °C, with the door left slightly open to provide sufficient air to oxidize the carbon. Heating is continued until the carbon is completely oxidized and a clean ash is obtained. The crucible and its contents are then removed from the furnace and allowed to cool to ambient temperature. 5 mL of nitric acid are added, and the resulting solution is transferred to a 50 mL volumetric flask and filled up with water to 50mL. 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 to be used, it has to be added.
before filling up: for a final volume of 50 mL, internal standard of 500 µL for ICP-OES, and 500 nL for ICP-MS, respectively, has to be added before filling up.

b) When sample contains significant amounts of halogen compounds (information may be available from previous screening experiments)
   — The sample is measured into a crucible. 10 to 15 mL of sulfuric acid is added, and the crucible and its contents are heated slowly on a hot plate or sand bath until the plastic melts and blackens. 5 mL of nitric acid are then added, and heating is continued until the plastic degrades completely and white fumes are generated.

c) After cooling, the crucible is placed in a muffle furnace maintained at 450 ± 25 °C and the sample is evaporated, dried, and ashed until the carbon has been completely incinerated. After ashing, 5 mL of nitric acid are added, and the resulting solution is transferred to a 50 mL volumetric flask and filled up with water to 50 mL. 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 to be used it has to be added before filling up: for a final volume of 50 mL, internal standard of 500 µL for ICP-OES, and 500 nL for ICP-MS, respectively has to be added before filling up.

d) If there are sample remnants, they are separated by a centrifuge or a filter. The residues have to be checked by appropriate measurements (e.g. XRF) in order to confirm the absence of the target elements.

NOTE: This method does not apply for fluorocarbons. See clause 11.1.

11.4.2.2 Acid digestion method

This method is used to determine cadmium only. It is not suited for determining lead, because the use of sulfuric acid can lead to a loss of lead in the sample due to the formation of lead sulfate.

a) The sample is measured into a flask. 5 mL of sulfuric acid and 1 mL of nitric acid are added and the flask is then heated until the sample ashes and white fumes are generated. Heating is stopped, nitric acid is added in small quantities (approx. 0.5 mL), and heating is continued until white fumes are generated. The above heating and decomposition with nitric acid is repeated until the decomposed solution turns pale yellow.

b) The sample is then allowed to cool down for several minutes. Hydrogen peroxide is added in small quantities, several milliliters at a time, and the sample is heated once again until white fumes are generated. After cooling, the solution is transferred to a 100 mL volumetric flask and the flask is then filled with water to 100 mL. 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 to be used it has to be added before filling up: for a final volume of 100 mL, internal standard of 1000 µL for ICP-OES, and 1000 nL for ICP-MS, respectively, has to be added before filling up.

c) When general digestion is inadequate or when the sample contains significant amounts of silica, titanium, etc. (information may be available from previous screening):
   — The sample is measured into a flask. 5 mL of sulfuric acid and 1 mL of nitric acid are added and the flask is then heated until the sample ashes and white fumes are generated. Heating is stopped, nitric acid is added in small quantities (approx. 0.5 mL), and heated is continued once again until white fumes are generated. The above heating and decomposition with nitric acid is repeated until the decomposed solution turns pale yellow.

   — The sample is then allowed to cool for several minutes. Hydrogen peroxide is added in small quantities, several milliliters at a time, and the sample is heated once again until white fumes are generated. After cooling, the solution is transferred to a fluorocarbon resin vessel. 5 mL of hydrofluoric acid is added and the vessel is heated until white fumes are generated. Boric acid may be added to permit the complexation of fluoride for protection of the quartz plasma torch (in case no acid resistant sample introduction system is available). After cooling, the solution is transferred to a 100 mL volumetric flask and the flask is then filled with water to 100 mL. 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 to be used it has to be added before filling up: for a final volume of 100 mL, internal standard (11.3 µL) of 1000 µL for ICP-OES, and 1000 nL for ICP-MS, respectively, has to be added before filling up.

d) If there are sample remnants, they are filtered using either a centrifuge or a filter. The residues have to be checked by appropriate measurements (e.g. XRF) in order to confirm the absence of the target elements.

11.4.2.3 Closed system for acid decomposition

a) The sample is measured into a microwave digestion vessel. 5 mL of nitric acid is added. The addition of hydrogen peroxide in small or catalytic quantities (such as 0.1 to 1 mL) may be performed as a support towards the complete oxidation of organic matter. The vessel is covered with a lid, and the vessel is placed in a microwave digestion device. The sample is digested in the microwave oven following a decomposition program specified in advance. After cooling, it is transferred to a 50 mL volumetric flask and the flask is then filled with water to 50 mL. 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 to be used it has to be added before filling up: for a final volume of 50 mL, internal standard of 500 µL for ICP-OES, and 500 nL for ICP-MS, respectively has to be added before filling up.

NOTE 1: The addition of hydrogen peroxide should only be done when the reactive components of the sample are known. Hydrogen peroxide may react rapidly and violently on easily oxidizable materials and should not be added when the sample might contain large quantities of easily oxidizable organic constituents.

b) When decomposition is inadequate or when the sample contains significant amounts of silica, titanium, etc. (Information may be available from previous screening):

— The sample is measured into a microwave digestion vessel. 5 mL of nitric acid and 1 mL of hydrofluoric acid are added. The addition of hydrogen peroxide in small or catalytic quantities (such as 0.1 to 1 mL) may be performed as a support towards the complete oxidation of organic matter. The vessel is covered with a lid, and the vessel is placed in a microwave digestion device. The sample is digested in the microwave oven following a decomposition program specified in advance. Boric acid may be added to permit the complexation of fluoride to protect the quartz plasma torch (in case no acid resistant sample introduction system is available). After cooling, the solution is transferred to a 50 mL volumetric flask and the flask is then filled with water to 50 mL. 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 to be used it has to be added before filling up: for a final volume of 50 mL, internal standard of 500 µL for ICP-OES, and 500 nL for ICP-MS, respectively has to be added before filling up.

NOTE 2: The addition of hydrogen peroxide should only be done when the reactive components of the sample are known. Hydrogen peroxide may react rapidly and violently on easily oxidizable materials and should not be added when the sample might contain large quantities of easily oxidizable organic constituents.

c) If there are sample remnants, they are filtered using either a centrifuge or a filter. The residues have to be checked by appropriate measurements (e.g. XRF) in order to confirm the absence of the target elements.

11.4.3 Preparation of laboratory reagent blank

Procedure identical to sample preparation is executed concurrently without sample.

11.5 Test Procedure

Typically, the sample should be assumed to consist of unknown composition. In this case, the internal standard method (intensity comparison method) is recommended. If necessary, standard addition 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 acid should also be adjusted to the samples concentration.
11.5.1 Preparation of calibration solution

After diluting each standard element solution gradually, the diluted standard solutions containing 0 - 100 µg of each element are transferred to a 100 mL volumetric flask. Next, each reagent and, in the case of internal standard method, the appropriate amounts of the solvents for the internal standard solutions are added to achieve reagent concentrations identical to those present in the sample solution. The resulting solution is the mixed calibration standard solution.

11.5.2 Development of calibration curve

The spectrometers are prepared for quantification. Some of the solution obtained in 11.5.1 is nebulized into the argon plasma or by acetylene/air flame, respectively. A hydrofluoric acid resistant sample introduction system has to be used when the sample solution contains hydrofluoric acid.

a) ICP-OES

— The readings for the emission intensity of the target elements (and, if required, that of the internal standard element) are determined. In the calibration curve method, the curve showing the relationship between the emission intensity of the target elements and their concentration is developed as the calibration curve. In the internal standard method, the curve showing the relation between intensity vs. concentration of the target elements with respect to that of the internal standard elements is developed as calibration curve.

— Recommended wavelengths and interfering elements are shown in clause 11.7, Table 11.

b) ICP-MS

— The readings for m/z of the target elements (and, if required, that of the internal standard element) are determined. In the calibration curve method, the curve showing the relationship between the intensities of m/z of the target elements and their concentration is developed as the calibration curve. In the internal standard method, the curve showing the relation between intensity vs concentration of the target elements with respect to that of the internal standard elements is developed as calibration curve.

— The mass/charge ratio may be defined based on the data shown in clause 11.7, Table 12.

c) AAS

— The readings for the absorption intensity of the target elements are determined. In the calibration method, the curve showing the relationship between the intensities of absorption intensity of the target elements vs. concentration is developed as the calibration curve.

— The wavelengths should be selected in regard to typical measurement wavelengths for elements shown in clause 11.7, Table 13. In the case of interference from co-present substances, either a wavelength that does not interfere with the calibration range has to be used or adjustments in the interference volume have to be made using a suitable method.

11.5.3 Measurement of 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 to the range of the calibration curve ensuring an appropriate acidification of the calibration standards and measured once again.

Measurement precision is checked with standard substance, calibration solution, etc., in regular intervals (such as once every 10 samples). If necessary, a calibration curve is developed again.
NOTE: If sample is diluted to the range of calibration, it has to be assured, that the internal standard concentration in the diluted sample solution is adjusted to the standard solution.

11.5.4 Calculation

The concentration measured in 11.5.3 is the concentration of each element in the sample solution. The concentration of each element in the sample is calculated from the equation:

Cadmium or lead (µg /g) = (A1 – A2) ×V / m

where A1 is the concentration of each target element in the sample solution in mg/L; A2, the concentration of each target element in the laboratory reagent blank in mg/L; V, the total volume for the sample solution in mL (depends on the particular series of dilutions taken); and m, the measured quantity of the sample in g.

11.6 Evaluation of the Method

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

11.7 Annex (Informative)

11.7.1 ICP-OES
Table 11: Spectral interferences for the wavelengths of cadmium and lead

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<th></th>
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<td>+</td>
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<td>+</td>
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</tbody>
</table>

The table shows the strength of interference for the wavelengths of Cd and Pb when 1000 mg/kg of the corresponding matrix elements are introduced:
- + no or small interference (typical less than 0.05 mg/kg)
- ++ medium interference (typical between 0.05 mg/kg and 0.2 mg/kg)
- +++ strong interference (typical more than 0.2 mg/kg)
11.7.2 ICP-MS

If a stable isotope is found, mass/charge number of a number of 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 12: Examples for mass-charge-ratios

<table>
<thead>
<tr>
<th>Element</th>
<th>Isotope</th>
<th>Isobar</th>
<th>Polyatomic ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>111Cd</td>
<td></td>
<td>MoO, MoOH, ZrOH</td>
</tr>
<tr>
<td></td>
<td>112Cd</td>
<td>Sn</td>
<td>MoO, MoOH</td>
</tr>
<tr>
<td></td>
<td>113Cd</td>
<td>In</td>
<td>MoO, MoOH, ZrOH, RuO</td>
</tr>
<tr>
<td></td>
<td>114Cd</td>
<td>Sn</td>
<td>MoO, MoOH, RuO</td>
</tr>
<tr>
<td>Pb</td>
<td>204Pb</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>206Pb</td>
<td>PtO</td>
<td></td>
</tr>
<tr>
<td></td>
<td>207Pb</td>
<td>IrO</td>
<td></td>
</tr>
<tr>
<td></td>
<td>208Pb</td>
<td>PtO</td>
<td></td>
</tr>
</tbody>
</table>

11.7.3 AAS

Recommended measurement wavelengths for AAS

Table 13: Examples for wavelengths for AAS

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength /nm</th>
<th>Slit width / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>228.8</td>
<td>0.7</td>
</tr>
<tr>
<td>Pb</td>
<td>261.4</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>217.0</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>283.3</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Light source: Electrodeless discharge lamp or hollow cathode lamp, Gas type: Acetylene/Air
12 Determination of Lead and Cadmium in Metals by ICP-OES, ICP-MS, and AAS

12.1 Scope, Application and Summary of Method

This document specifies the procedure for the determination of lead (Pb) and cadmium (Cd) in metals from electrotechnological equipment. The document describes the use of three methods (ICP-OES, ICP-MS and AAS). The samples are digested with acids such as hydrochloric acid or nitric acid. Subsequently the lead and cadmium in the solutions thus obtained are determined either by ICP-OES, by ICP-MS, or by AAS, respectively. The detailed procedures depend on the matrix and on the presence of particular elements as well and are described in the text. Procedures are given for the case of unknown samples and of samples, where screening methods already indicate 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 that range for ICP-OES and AAS from 10 mg/kg for cadmium and 100 mg/kg for lead and for ICP-MS from 0.1 mg/kg for cadmium and lead. The procedures are not limited for higher concentrations.

Limitations and risks occur due to the solution step of the sample, e.g.: 1) precipitation of the target or of other elements (risk of co-precipitation) may occur; in this case the remnants have to be checked separately or dissolved by another way and then fused with the test sample solution; 2) evaporation of 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. microwave digestion system is strongly advised. However, if the experts can assure its suitability, simple alternatives may be used. Detailed information is given within the text.

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

12.2 Apparatus/Equipment and Materials

a) Scale: Precision level of 0.1 mg  
b) Glassware: All glassware shall be cleaned with 10 % (m/m) nitric acid before use  
   — Beakers: Such as 100 mL, 200 mL, 500 mL, etc.  
   — Volumetric flasks: Such as 100 mL, 200 mL, 500 mL, etc.  
   — Pipettes: Such as 1 mL, 5 mL, 10 mL, 20 mL, etc.  
   — Watch glass  
c) Micropipettes: Such as 200 µL, 500 µL, 1000 µL, etc.  
d) Poly(tetrafluoroethylene) (PTFE) / Perfluoroalkoxy (PFA) equipment: All equipment shall be cleaned with 10 % (m/m) nitric acid before use  
   — Beaker: Such as 100 mL, 200 mL, 500 mL, etc.  
   — Cover for Beaker  
   — Volumetric flasks: Such as 100 mL, 200 mL, 500 mL, etc.  
e) 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.  
f) Containers: For storage of standard solution and calibration standard  
   — Containers to be made of high-density polyethylene (HDPE) or PFA bottles  
g) Electric hot plate or heated sand bath  
h) ICP-OES: Apparatus consisting of excitation source, sample holder, light source, spectrophotometer, data processor and control system.
i) ICP-MS: Apparatus consisting of sample holder, ionizer, spray chamber, nebulizer interface, ion lens, mass separator, detector, evacuated vessel, system control and data output device.

j) AAS: Apparatus consisting of a single–slot burner head, hollow cathode lamps, detector, data processor and control system.

k) Hydrofluoric acid resistant sample holder: Sample holder of which the sample insertion section and torch have been treated for resistance against hydrofluoric acid.

l) Argon gas: Gas with purity of over 99.99 % (v/v)

m) Acetylene gas: Gas with purity of over 99.99 % (v/v)

12.3 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 should be negligible compared to the lowest concentration to be determined.

All reagents for ICP-MS analysis including acids or chemicals in use should be high purity ones: trace metals in total less than $1 \times 10^{-6}$ % (m/m).

a) Water: Grade 1 specified in ISO 3696:1987 used for preparation and dilution of all sample solutions.

b) Hydrochloric acid: $\rho$(HCl) = 1.16 g/mL

c) Nitric acid: $\rho$(HNO$_3$) = 1.4 g/mL

d) Nitric acid: Dilution (1+ 2): Dilute 1 volume of concentrated nitric acid (12.3 c)) with 2 volumes of water (12.3 a))

e) Perchloric acid: $\rho$(HClO$_4$) =1.67 g/mL, 70 % (m/m)

f) Phosphoric acid: $\rho$(H$_3$PO$_4$) =1.69 g/mL, more than 85 % (m/m)

g) Sulfuric acid: $\rho$(H$_2$SO$_4$) = 1.84 g/mL

h) Sulfuric acid: Dilution (1+ 2): Dilute 1 volume of concentrated sulfuric acid (12.3 g)) with 2 volumes of water (12. 3 a))

i) $\rho$(HF) = 1.18 g/mL (50 % (m/m))

j) Hydrobromic acid: $\rho$(HBr) = 1.48 g/mL, 47~49 % (m/m)

k) Mixed acid 1 (two parts hydrochloric acid, one part nitric acid and two parts water)

l) Mixed acid 2 (one part nitric acid and three parts hydrofluoric acid)

m) Mixed acid 3 (three parts hydrochloric acid and one part nitric acid)

n) Standard solution with 1000 µg/L of lead

o) Standard solution with 1000 µg/L of cadmium

p) Internal standard solution

— Internal standard elements that do not interfere with the target element will be used. 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.

NOTE 1: The toxicity of each reagent used in this method has not been precisely defined; however, each chemical compound needs to be treated as a potential health hazard. From this viewpoint, exposure to these chemicals to 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 spectacles should be worn when handling acids.

NOTE 3: Toxic fumes are evolved by nitric acid. Always carry out digestion in a fume cupboard, as well as addition of 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 precaution measures should be taken in case that hydrofluoric acid or perchloric acid (requires special hood, risk of explosion) is used i.e. HF antidote gel for first aid treatment of HF burns on the skin.
12.4 Sample Preparation

12.4.1 Test portion

1 g of sample is measured accurately to the 0.1 mg level and is placed into a glass beaker or, when using hydrofluoric acid, PTFE/PFA beaker.

12.4.2 Preparation of test sample solution

Preparation of a test sample solution herein does not necessarily cover all metals and their compounds. Generally speaking, preparation of solution with hydrochloric acid, nitric acid or mixture thereof is recommended. Samples that are difficult to dissolve with these acids should have perchloric acid, sulfuric acid, etc., added as necessary. Please keep in mind that the use of sulfuric acid is critical in the determination of lead due to the risk of losing some of the target analyte. Samples should be dissolved completely without any remains under heating at high temperatures. A sample may also be dissolved by using phosphoric acid.

In dissolving metals or especially mixtures thereof by strong acids, there is always a risk of precipitation (e.g.: Pb and Ba with sulfuric acid, Ag with hydrochloric acid, Al may form oxides/oxide-hydrates and the like). Even if these elements often are not covered by legislation, there is the risk of loss of target analyte due to co-precipitation. For this standard it has to be assured that no target elements are lost in the test sample solution. So any remnants have to be checked either by different methods, whether they contain target elements or the remnants after acid dissolution are to be dissolved completely by further dissolution methods (such as alkali fusion or use of an airtight pressurized vessel). The so treated, formerly remnants are then combined with acid-dissolved solution for measurement.

a) Common methods for sample digestion

— A glass beaker containing the sample is covered with a watch glass. 20 mL of mixed acid 1 is added and the beaker is heated until the sample has been dissolved. After cooling to room temperature, the underside of the watch glass and inside wall of the beaker are rinsed with water, and the watch glass is removed. The solution is transferred to a 100 mL volumetric flask and the flask then filled with water to 100 mL. The resulting solution is the concentrate sample solution. The concentrate sample solution is diluted with water to the appropriate concentration level for each measurement apparatus. If necessary, an internal standard element, rhodium, for example, is added before the flask is filled with water. The type of element and its amount depend on the analytical method selected. The particular paths of dilution have to be taken into account in the calculation of results. Both, dilution and internal standard addition have to be documented in the test report.

b) If containing zirconium, hafnium, titanium, tantalum, niobium or tungsten

— A PTFE/PFA beaker containing the sample is covered. 20 mL of mixed acid 2 is added and the beaker is heated until the sample is dissolved. After cooling to room temperature, the underside of the cover and inside wall of the beaker are rinsed with water, and the cover is removed. The solution is transferred to a 100 mL volumetric flask and the flask is filled with water to 100 mL. The resulting solution is the concentrate sample solution. The concentrate sample solution is diluted with water to the appropriate concentration level for each measurement apparatus. If necessary, an internal standard element, rhodium, for example, is added before the flask is filled with water. Because of the use of hydrofluoric acid, the internal standard should not comprise rare earth elements. The type of element and its amount depend on the analytical method selected. The particular paths of dilution have to be taken into account in the calculation of results. Both, dilution and internal standard addition have to be documented in the test report.

c) If containing tin

— A beaker containing the sample is covered. 10 mL of mixed acid 3 is added in small quantities. After violent reaction ends, the beaker is heated slowly until the sample is dissolved completely. After cooling, the underside of the cover and inside wall of the beaker are rinsed with water, and the cover is removed. 10 mL of sulfuric acid is added
and the beaker is heated until white fumes of SO$_3$ are liberated. After cooling for several minutes, 20 mL of hydrobromic acid are added, and the beaker is heated until white fumes are visible. This process is repeated three times. After cooling to room temperature, 10mL of nitric acid is added to dissolve salts. After cooling to room temperature, the solution is transferred to a 100 mL volumetric flask which is then filled with water to 100 mL. The resulting solution is the concentrate sample solution. The concentrate sample solution is diluted with water to the appropriate concentration level for each measurement apparatus. If necessary, an internal standard element, rhodium, for example, is added to the flask before filling with water. The type of element and its amount depend on the analytical method selected. The particular paths of dilution have to be taken into account in the calculation of results. Both, dilution and internal standard addition have to be documented in the test report.

d) If there are sample remnants, they are separated by a centrifuge or a filter. The residues have to be checked by appropriate measurements (e.g. XRF) in order to confirm the absence of the target elements.

NOTE: If containing a large quantity of tin in the presence of silver i.e. lead free solder, the dissolving acid should be hydrochloric acid followed by 10 mL successive addition of Hydrogenperoxid until complete digestion.

12.5 Preparation of laboratory reagent blank

Procedure identical to preparation of test sample solution is executed concurrently without sample.

12.6 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 employed (not suitable for AAS). If required, the standard-additions method also may be used.

Note 1: High matrix concentration samples are recommended to employ the matrix matching method. In all cases, acid should also be adjusted to the samples 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.

12.6.1 Preparation of calibration standard

a) Calibration method (Matrix matching method)

— After diluting each standard element solution gradually, the diluted standard solutions containing 0 – 100 µg of each element are transferred to 100 mL volumetric flasks. For the matrix matching method, a close matrix matching of the standard solution is necessitated. In this case, the matrix elements either should be known (e.g. from previous documented spec) or evaluated by previous screening experiments using XRF. Each reagent and the matrix (elements) are added in order to prepare mixed calibration standards that are equivalent to that of the sample solution.

— When hydrofluoric acid is used, a PTFE/PFA beaker and high-density polyethylene volumetric flask or PTFE/PFA volumetric flask are used.

b) Internal standard method

— Each standard element solution is added in steps in 100 mL measuring flasks. In order to achieve concentrations equivalent to that of the sample solution, reagents and internal standard elements are added to prepare mixed calibration standard solutions.

— If using hydrofluoric acid, a PTFE/PFA beaker and high-density polyethylene volumetric flask or a PTFE/PFA volumetric flask have to be taken.

12.6.2 Measurement of calibration standard

a) ICP-OES
Some part of the calibration solutions prepared as described in 12.5.1 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 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 element with respect to the internal standard element is developed as the calibration curve.

A hydrofluoric acid resistant sample holder and torch has to be used when the solution contains hydrofluoric acid.

The recommended wavelength is selected from the spectral lines for each element. The wavelength should be selected in regard to typical measurement wavelengths for elements shown in clause 12.8, Table 14. Thorough study on detection limit, measurement precision, etc., have to be conducted. In the case of interference from co-present substances, either a wavelength that does not interfere with the calibration range has to be selected or adjustments in interference volume have to be made using a suitable method.

b) ICP-MS

The ICP mass spectrometer is prepared for quantification. Some of the solution obtained in 12.5.1 is nebulized into the argon plasma through the sample holder. A hydrofluoric acid resistant sample holder has to be used when the solution contains hydrofluoric acid. The readings for m/z of the target elements and internal standard element are determined, and the ratio of the reading for the target element and the reading for internal standard element is calculated. The mass-charge-ratios may be defined based on the measured mass numbers shown in Table 15.

c) AAS

Portions of the calibration solutions prepared as described in 12.5.1 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 concentration is developed as the calibration curve.

The wavelengths should be selected in regard to typical measurement wavelengths for elements shown in Table 16. In the case of interference from co-present substances, either a wavelength that does not interfere with the calibration range has to be used or adjustments in the interference volume have to be made using a suitable method.

12.6.3 Measurement of sample

After the calibration curve is plotted, 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 calibration standards and measured once again.

The measurement precision is checked with standard substance, calibration solution, etc., in regular intervals (such as once every 10 samples). If necessary, a calibration curve has to be developed again.

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

12.6.4 Calculation

The spectrometer readings of each sample as obtained according to 12.5.3 and the calibration curve developed as described in 12.5.2 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:

\[
\text{Cadmium or lead (µg/g)} = (A_1 - A_2) \frac{V}{m}
\]
where $A_1$ is the concentration of each target element in the sample solution in mg/L; $A_2$, the concentration of each target element in the laboratory reagent blank in mg/L; $V$, the total volume for the sample solution in mL (depends on the particular series of dilutions taken); and $m$, the measured quantity of the sample in g.

12.7 Evaluation of the Method

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

12.8 Annex (Informative)

12.8.1 ICP-OES
### Table 14: Spectral interferences for the wavelengths of cadmium and lead

<table>
<thead>
<tr>
<th>(nm)</th>
<th>Cd</th>
<th>Cd</th>
<th>Cd</th>
<th>Cd</th>
<th>Pb</th>
<th>Pb</th>
<th>Pb</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>214,439</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>226,502</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>228,802</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>361,051</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>217,000</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>220,353</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>261,417</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>283,305</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

The Table shows the strength of interference for the wavelengths of Cd and Pb when 1000 mg/kg of the corresponding matrix elements are introduced:

- **+** no or small interference (typical less than 0.05 mg/kg)
- **++** medium interference (typical between 0.05 mg/kg and 0.2 mg/kg)
- **+++** strong interference (typical more than 0.2 mg/kg)

**Background correction**

In the case of changing background by the main matrix of solution and affecting the emission intensities (lx), the emission intensities should be obtained by deducting the background.
intensities (I(x')). Figure 6 shows one example of the effect of background correction. Figure 6(a) shows the example of uniform background versus wavelength. In this case, background could be corrected by both of position A and B. Figure 6(b) shows the example of changing background versus wavelength. In this case, background intensities should be corrected by obtaining the background intensities (I(x')), which are calculated by both position A and position B of emission intensities.

**Figure 6: Background Correction**

Depending on the equipment, alternatively standard addition may be used (instead of background correction).

12.8.2 ICP-MS

If a stable isotope is found, mass/charge number of a number of 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 15: Examples for mass-charge-ratios

<table>
<thead>
<tr>
<th>Element</th>
<th>Isotope</th>
<th>Isobar</th>
<th>Polyatomic ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>111Cd</td>
<td></td>
<td>MoO, MoOH, ZrOH</td>
</tr>
<tr>
<td></td>
<td>112Cd</td>
<td>Sn</td>
<td>MoO, MoOH</td>
</tr>
<tr>
<td></td>
<td>113Cd</td>
<td>In</td>
<td>MoO, MoOH, ZrOH, RuO</td>
</tr>
<tr>
<td></td>
<td>114Cd</td>
<td>Sn</td>
<td>MoO, MoOH, RuO</td>
</tr>
<tr>
<td>Pb</td>
<td>204Pb</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>206Pb</td>
<td>PtO</td>
<td></td>
</tr>
<tr>
<td></td>
<td>207Pb</td>
<td>IrO</td>
<td></td>
</tr>
<tr>
<td></td>
<td>208Pb</td>
<td>PtO</td>
<td></td>
</tr>
</tbody>
</table>

12.8.3 AAS

Recommended measurement wavelengths for AAS.

Table 16: Examples for wavelengths for AAS

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength /nm</th>
<th>Slit width / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>228.8</td>
<td>0.7</td>
</tr>
<tr>
<td>Pb</td>
<td>261.4</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>217.0</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>283.3</td>
<td>0.7</td>
</tr>
</tbody>
</table>
13 Determination of Lead and Cadmium in Electronics by ICP-OES, ICP-MS, and AAS

13.1 Scope, Application and Summary of Method

This document specifies the procedure for the determination of lead (Pb) and cadmium (Cd) in electronics (printed circuit boards or single components from electrical and electronic equipment). The document describes the use of three methods (ICP-OES, ICP-MS and AAS) and several procedures for preparing the sample solution, from which the most appropriate way of analysis can be selected by the experts.

The samples for investigation have to be available as ground material of the electronics, as described in clause 5. The powder is either digested with aqua regia or microwave-enhanced with HNO\textsubscript{3}, HBF\textsubscript{4}, H\textsubscript{2}O\textsubscript{2} and HCl. The aqua regia digestion procedure is attributed to DIN EN ISO 5961. Subsequently in the obtained digestion solution the elements lead and cadmium are determined simultaneously either by ICP-OES or by ICP-MS or one element after the other by AAS.

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 for ICP-OES and AAS from 10 mg/kg for cadmium and 100 mg/kg for lead and for ICP-MS from 0.1 mg/kg for cadmium and lead. The procedures are not limited for higher concentrations.

The analysis by ICP-OES, ICP-MS or AAS allows the determination of the target elements with high precision (uncertainty in the low percentage range) and/or high sensitivity. These advantages may be limited, when the samples to be analyzed have a highly complex composition. Samples shall be destroyed by appropriate mechanical means prior to the chemical digestion. The correct grain size as a function of the amount of starting material is essential. In order to fulfill minimum requirements for a correct analysis, maximum grain size and minimum amounts of sample are given within the text. It is highly likely that after the digestion methods solid residues are present. It has to be assured (e.g. by using XRF) that there are no target elements in considerable amounts in the residues. Alternatively they have to be resolved by different chemical approaches and combined to the test sample solution. This standard strongly recommends the use of sophisticated equipment i.e. microwave digestion system for the digestion methods. Nevertheless, if the user assures suitability of a simpler approach, the later may be applied. Any deviation from the described procedures has to be evaluated and documented in the test report.

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

13.2 Apparatus / Equipment and Materials

a) ICP-OES: Inductively Coupled Plasma Optic Emission Spectrometer, equipped with sequential optic or with polychromators.

b) ICP-MS: Inductively Coupled Mass Spectrometer, equipment consisting of sample holder, ionizer, interface, ion lens, mass separator, detector, evacuated vessel, system control and data output device.

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

d) Argon gas: gas with purity of over 99.99 % (v/v)

e) AAS: Atomic absorption spectrometer, equipped with a single-slot burner head for air-acetylene flame AAS (FAAS) operations, hollow cathode lamps for cadmium and lead.

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 TFM-PTFE-vessels with a capacity of 40mL.

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

i) Scale: Precision level of 0.1 mg

j) Glassware: All glassware shall be cleaned with 10 % (m/m) nitric acid before use
   - Beakers: Such as 100 mL, 200 mL, 500 mL, etc.

k) Volumetric flasks: Such as 100mL, 200mL, 500mL, etc
   Where appropriate, other types of volumetric equipment with acceptable precision and accuracy can be used as an alternative to volumetric flasks.
   - Pipettes: Such as 1 mL, 5 mL, 10 mL, 20 mL, etc.
   - Graduated cylinder
   - Watch glass

l) Micropipettes: Such as 200 µL, 500 µL, 1000 µL, etc.

m) PTFE/PFA containers: All equipment shall be cleaned with 10 % (m/m) nitric acid before use
   - Beakers: Such as 100 mL, 200 mL, 500 mL, etc.
   - Volumetric flasks: Such as 100 mL, 200 mL, etc.

n) Containers: For storage of standard solution and calibration standard
   Containers made of high-density polyethylene to be used for ordinary measurement of element concentration. For determination on the ultratrace level, containers made of perfluoralkoxy (PFA) or fluorinated ethylene-propylene copolymer (FEP). In either case, the user shall confirm the suitability of the container selected.

o) Electric hot plate or heated sand bath

p) Microwave digestion vessel: Such as 40 mL, 100 mL, etc.

q) Filter:
   - Glass fiber filter 0.45 µm (digestion with aqua regia)
   - Whatman filter 0.45 µm (microwave digestion)

13.3 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 should be negligible compared to the lowest concentration to be determined.

All reagents for ICP-MS analysis including acids or chemicals in use should be high purity ones: trace metals in total less than 1×10^{-6} % (m/m).

a) Water: Grade 1 specified in ISO 3696:1987 used for preparation and dilution of all sample solutions

b) Hydrochloric acid: ρ(HCl) = 1.16 g/mL, 37 % (m/m)

c) Hydrochloric acid: Dilution (1+ 2): One part hydrochloric acid (13.3 b)) diluted with two parts water (13.3 a)).

d) Nitric acid: ρ(HNO₃) =1.4 g/mL, 65 % (m/m)

e) Mixed acid (3 parts hydrochloric acid and 1 part nitric acid)

f) Tetrafluoroborate solution, HBF₄, 40 % (m/m)
g) Hydrogen peroxide $\text{H}_2\text{O}_2$, 30 % (m/m), p.a. grade

h) Standard solution with 1000 $\mu$g/g of lead

i) Standard solution with 1000 $\mu$g/g of cadmium

j) Standard solution with 10 000 $\mu$g/g of copper

k) Standard solution with 10 000 $\mu$g/g of iron

l) Internal standard solution: Internal standard elements that do not interfere with target element should be used. Also, the presence of these internal standard elements in the sample solution shall be on the 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 needs to be treated as a potential health hazard. From this viewpoint, exposure to these chemicals to 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 spectacles should be worn when handling acids.

NOTE 3: Toxic fumes are evolved by nitric acid. Always carry out digestion in a fume cupboard, as well as addition of 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 precaution measures should be taken in case that hydrofluoric acid or perchloric acid (requires special hood, risk of explosion) is used i.e. HF antidote gel for first aid treatment of HF burns on the skin.

13.4 Sample Preparation

Preparation of a test sample solution herein does not necessarily cover all electronics and their compounds. Generally speaking, preparation of solution with hydrochloric acid, nitric acid or mixture thereof is recommended. Samples that are difficult to dissolve with these acids should have perchloric acid, sulfuric acid, etc., added as necessary. Please keep in mind that the use of sulfuric acid is critical in the determination of lead due to the risk of loosing some of the target analyte. Samples should be dissolved completely without any remains under heating at high temperatures.

In dissolving metals or especially mixtures thereof by strong acids, there is always a risk of precipitation (e.g: Pb and Ba with sulfuric acid, Ag with hydrochloric acid, Al may form oxides/oxide-hydrates and the like). Even if these elements often are not covered by legislation, there is the risk of loss of target analyte due to co-precipitation. For this standard it has to be assured that no target elements are lost in the test sample solution. So any remnants have to be checked either by different methods, whether they contain target elements or the remnants after acid dissolution are to be dissolved completely by further dissolution methods (such as alkali fusion or use of an airtight pressurized vessel). The so treated, formerly remnants are then combined with acid-dissolved solution for measurement.

13.4.1 Test portion

The different analytical procedures, which can be used alternatively according to this standard, need different amounts of sample in order to achieve the required quality of results. In the case of electronics, the sample first shall be destroyed mechanically by appropriate means (e.g. grinding, milling, mill-cutting) before chemical dissolution of the powder can start. In order to assure a representative sample taking at this step, a certain grain 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 the use in ICP-MS.

13.4.2 Digestion with aqua regia

Approximately 2 g of the ground sample (maximum grain size: 250 $\mu$m) is weighed into the reaction vessel and 22.5 mL HCl (37 % (m/m)) and 7.5 mL HNO$_3$ (65 % (m/m)) are added. The vessel is furnished with a reflux cooler and an absorption vessel containing 10 mL 0.5 Mol/L HNO$_3$, before a temperature program is started to digest the samples for 12 h at room temperature and for 2 h at 120 °C. After cooling to room temperature, the content of the
absorption tube is put into the reaction vessel, the sample is filtered over a 0.45 µm filter and the solid residue is washed four times with 15 mL 5 % (m/m) HCl. The obtained solution is transferred into a 250 mL volumetric flask and filled up with 5 % (m/m) HCl 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 to be used, it has to be added before filling up: for a final volume of 100 mL, internal standard of 1000 µl for ICP-OES, and 1000 nL for ICP-MS, respectively, has to be added before filling up.

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

In case the lab does not have the above described recommended equipment, it may be possible to use a simpler approach, when the user can assure the suitability of his approach. Deviations from the above described procedure 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 containing the sample is covered with a watch glass. Mixed acid (3 parts HCl + 1 part HNO₃) is added and the beaker is heated for 2 hours at 120 °C and then allowed to stand for 12 hours at room temperature. The underside of the watch glass and inside wall of the beaker are rinsed with water, and the watch glass is removed. After cooling, the sample is filtered with a 0.45 µm membrane filter. The remnants are rinsed with hydrochloric acid. The solution is transferred to a volumetric flask and the flask is filled with water. The resulting solution is used for further measurements.

13.4.3 Microwave digestion

300 mg of ground sample (maximum grain size: 250 µm) is weighed into a PTFE-TFE or a PTFE/PFA vessel. 4 mL of nitric acid, 2 mL of tetrafluoroborate, 1mL of hydrogen peroxide and 1 mL of water 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 following a digestion program specified in advance. During these digestion step A, organic components such as polyvinyl chloride and in addition some of the metal elements are dissolved.

The vessel is opened after cooling to room temperature (approximately required time: 1 h), and 4 mL HCl (37 % (m/m)) are added. After sealing again, further elements are dissolved by HCl during a second microwave enhanced digestion step (step B). An example for a suitable microwave program (steps A and B) is given in clause 13.7 (Table 17).

After cooling the vessel to room temperature again (approximately required time: 1 h), it is opened and the solution is filtered over a Whatman filter into a 25 mL flask, washed and filled to the mark with 5 % (m/m) HCl. If there are sample remnants on the filter, they have to be checked by appropriate measurements (e.g. XRF) in order to confirm the absence of the target elements.

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

NOTE 1: It is highly recommended not to weigh in more than 300 mg of ground sample into the digestion vessel. Powdered electronics with mixtures of nitric acid, tetrafluoroborate, hydrogen peroxide and hydrochloric acid may react rapidly and violently under formation of gas (CO₂, NOₓ, etc.). This causes an increase in pressure in the closed vessel. By sudden development of pressure, the safety system of the microwave oven reacts and opens the vessel. Thus target elements might get lost and in worst case an explosion can happen.

NOTE 2: Also weigh in same sample amounts and same type of samples when duplicating or triplicating the analysis in one run.

If a sample amount of more than 300 mg is necessary to guarantee the representativeness, the following has to be done: Divide the sample into portions of identical weight. Weigh in
each portion into one digestion vessel, follow the digestion procedure and combine the obtained digestion solutions.

Example: For the digestion of a printed wiring board a minimum sample amount of 1.2 g is needed. Therefore 4 x 300 mg of ground sample has to be weighed into four vessels. After cooling at the end of microwave program B, the vessels are opened, the solutions are combined by filtering over a Whatman filter (0.45 µm) into a 100 mL volumetric flask, washed and filled to the mark with 5 % (m/m) HCl.

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

13.5 Test Procedure

The calibration curve method is used for sample measurement. Electronics (PCBs / single components) are samples with a complex matrix for the analytical methods in this standard, even after sample preparation. After the digestion (aqua regia or microwave), the solutions have, for example, high contents 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-additions 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.

13.5.1 Preparation of calibration solution

a) Calibration method (Matrix matching method)

— After diluting each standard element solution gradually, the diluted standard solutions containing 0 – 100 μg of each element are transferred to 100 mL volumetric flasks. For matrix matching method, a close matrix matching of standard solution is necessitated. The matrix elements are identified by previous XRF screening. In order to achieve equivalent to that of the sample solution, reagent and matrix elements are added to prepare mixed calibration standard solutions. The resulting solution is the mixed calibration solution.

— If using tetrafluoroborate, a high-density polyethylene volumetric flask or a PTFE/PFA volumetric flask has to be taken.

b) Internal standard method

— Each standard element solution is added in steps in 100 mL measuring flasks. In order to achieve concentrations equivalent to that of the sample solution, reagents and internal standard elements are added to prepare mixed calibration standard solutions.

— If using tetrafluoroborate, a high-density polyethylene volumetric flask or a PTFE/PFA volumetric flask has to be taken.

c) ICP-OES, AAS: The high iron and copper content necessitates a close matrix matching of standard solutions and an appropriate line selection. Therefore the calibration should be done using matrix adjusted calibration solutions. Recommended wavelengths can be found in clause 13.7.

d) ICP-MS: Here the use of an appropriate internal standard is recommended. Clause 13.7 gives the recommended m/z for the measurements together with potential interferences.

13.5.2 Standard preparation

a) ICP-OES, AAS

— Sample solutions obtained from aqua regia digestion have another matrix composition as solutions from 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 Cd and Pb are in the linear
range. Calibration blank and four calibration standards are prepared as calibration solutions.

b) Aqua regia digestion standards

- Calibration blank: 100 mL 10 % (m/m) HCl
- Calibration standards 1 to 3 (100 mL in each case): Solutions containing 1500 µg/mL Fe and 1500 µg/mL Cu, 24 mL HCl 37 % (m/m) 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.

c) Microwave digestion standards

- Calibration blank: Mixture of 92 mL 10 % (m/m) HCl and 8 mL HBF₄ 50 % (m/m)
- Calibration standards 1 to 3 (100 mL in each case): containing 1500 mg/L Fe and 1500 µg/mL Cu, 24 mL HCl 37 % (m/m), 8 mL HBF₄ and Pb and Cd in different concentrations. 1.2 µg/mL target element in solution corresponds to 100 µg/g target element in electronics.

d) ICP-MS

- Calibration blank and three calibration standards are prepared as calibration solutions.
- After diluting each standard element solution gradually, the solutions are transferred to 100 mL measuring flasks with 0-5 µg of each element. Next, each reagent and 1 µg of rhodium solvent are added to achieve reagent concentrations identical to that of the sample solution, and mixed calibration standard solution is prepared.

13.5.3 Calibration

a) ICP-OES, AAS

- The calibration blank and standard solutions are measured by ICP-OES or AAS and linear calibration plots for lead and cadmium are set up.

b) ICP-MS

- The ICP mass spectrometer is prepared for quantification. Some of the solution obtained in 13.7.1 is nebulized into the argon plasma through the sample holder. The readings for m/z of the target elements and rhodium are determined, and the ratio of the reading for the target element and the reading for the rhodium is calculated.
- The hydrofluoric acid resistant sample introduction system has to be used when the sample contains tetrafluoroborate.

13.5.4 Development of calibration curve

a) ICP-OES(-OES)

- Some part of the calibration solutions prepared as described in 13.5.1 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 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 element with respect to the internal standard element is developed as the calibration curve.
- A hydrofluoric acid resistant sample introduction system and torch has to be used when the solution contains hydrofluoric acid.
- The recommended wavelength is selected from the spectral lines for each element. The wavelength should be selected in regard to typical measurement wavelengths for elements shown in Table 18. Thorough study on detection limit, measurement precision, etc., have to be conducted. In the case of interference from co-present substances, either a wavelength that does not interfere with the calibration range has to be selected or adjustments in interference volume have to be made using a suitable method.
b) ICP-MS

The ICP mass spectrometer is prepared for quantification. Some of the solution obtained in 13.5.1 is nebulized into the argon plasma through the sample holder. A hydrofluoric acid resistant sample holder has to be used when the solution contains hydrofluoric acid. The readings for m/z of the target elements and internal standard element are determined, and the ratio of the reading for the target element and the reading for internal standard element is calculated. The mass-charge-ratios may be defined based on the measured mass numbers shown in clause 13.7, Table 19.

c) AAS

Portions of the calibration solutions prepared as described in 13.5.1 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 concentration is developed as the calibration curve.

The wavelengths should be selected in regard to typical measurement wavelengths for elements shown in clause 13.7 (Table 20). In the case of interference from co-present substances, either a wavelength that does not interfere with the calibration range has to be used or adjustments in the interference volume have to be made using a suitable method.

13.5.5 Measurement of sample

After the calibration curve is 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 with standard substance, calibration solution, etc., in regular intervals (such as once every 10 samples). If necessary, a calibration curve has to be developed again.

13.5.6 Calculation of Analytical Results

The spectrometer readings of each sample as obtained according to 13.5.3 and the calibration curve developed as described in 13.7.2 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:

\[ \text{Lead or cadmium } \mu g / g = (A1 - A2) \frac{V}{m} \quad (\text{Eq. 1}) \]

where \( A1 \) is concentration of each target element in the test sample solution in \( \mu g/mL \); \( A2 \), the concentration of each target element in the laboratory reagent blank in \( \mu g/mL \); \( V \) the volume of the concentrate sample solution in mL, and \( m \), the measured mass of sample in g.

NOTE: Due to the potential variation in analytical paths according to this standard, allowing individual dilutions of the starting test sample solution, Eq. 1 gives only the general approach. It has to be assured individually that all dilutions have been taken into account for the calculation of the result.

13.6 Evaluation of the Method

The precision and accuracy of the methods, the detection limits of the methods, and the way how to assure these qualities of data and determination process will be updated here once the suitable amounts of data become available from volunteer laboratories chosen by IEC TC111 WG3.
13.7 Annex (Informative)

Table 17: Program for microwave digestion of samples (power output for five vessels)

<table>
<thead>
<tr>
<th>Step</th>
<th>Time (min)</th>
<th>Power output (W)</th>
<th>Pressure limited to (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>5</td>
<td>300</td>
<td>2.5</td>
</tr>
<tr>
<td>2A</td>
<td>5</td>
<td>350</td>
<td>2.5</td>
</tr>
<tr>
<td>3A</td>
<td>17</td>
<td>450</td>
<td>2.5</td>
</tr>
<tr>
<td>4A</td>
<td>2</td>
<td>300</td>
<td>2.5</td>
</tr>
<tr>
<td>Ventilation step A</td>
<td>3</td>
<td>0</td>
<td>2.5</td>
</tr>
<tr>
<td>1B</td>
<td>5</td>
<td>300</td>
<td>2.5</td>
</tr>
<tr>
<td>2B</td>
<td>5</td>
<td>400</td>
<td>2.5</td>
</tr>
<tr>
<td>3B</td>
<td>17</td>
<td>450</td>
<td>2.5</td>
</tr>
<tr>
<td>Ventilation step B</td>
<td>3</td>
<td>0</td>
<td>2.5</td>
</tr>
</tbody>
</table>

13.7.1 ICP-OES(-OES)
Table 18: Recommended wavelengths and interfering elements (Spectral interferences for the wavelengths of cadmium and lead)

<table>
<thead>
<tr>
<th></th>
<th>Cd</th>
<th>Cd</th>
<th>Cd</th>
<th>Cd</th>
<th>Pb</th>
<th>Pb</th>
<th>Pb</th>
<th>Pb</th>
</tr>
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<tbody>
<tr>
<td>(nm)</td>
<td>214,439</td>
<td>226,502</td>
<td>228,802</td>
<td>361,051</td>
<td>217,000</td>
<td>220,353</td>
<td>261,417</td>
<td>283,305</td>
</tr>
<tr>
<td>Ag</td>
<td>+</td>
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<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
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<td>+</td>
</tr>
<tr>
<td>As</td>
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<td>+</td>
<td>+++</td>
<td>+</td>
<td>+</td>
<td>+</td>
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<tr>
<td>Au</td>
<td>+</td>
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<td>++</td>
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</tr>
<tr>
<td>Ca</td>
<td>+</td>
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<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Co</td>
<td>+</td>
<td>++</td>
<td>+++</td>
<td>+++</td>
<td>++</td>
<td>+++</td>
<td>+++</td>
<td>++</td>
</tr>
<tr>
<td>Cr</td>
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<td>+</td>
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<td>+</td>
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<tr>
<td>Cu</td>
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<td>+</td>
<td>+</td>
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<td>+++</td>
<td>+</td>
<td>+</td>
<td>+++</td>
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<tr>
<td>Ga</td>
<td>+</td>
<td>+</td>
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<td>+</td>
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<tr>
<td>Ge</td>
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<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
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<td>++</td>
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<td>++</td>
<td>+++</td>
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<tr>
<td>Mg</td>
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</tr>
<tr>
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</tr>
<tr>
<td>Mo</td>
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</tr>
<tr>
<td>Ni</td>
<td>+</td>
<td>+</td>
<td>++</td>
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<tr>
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<td>+</td>
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<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Sb</td>
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<tr>
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<td>+++</td>
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<td>+</td>
<td>+</td>
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<td>++</td>
<td>+</td>
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</tr>
<tr>
<td>W</td>
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<td>+++</td>
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<td>+++</td>
<td>+</td>
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</tr>
<tr>
<td>Zn</td>
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<td>+</td>
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<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Al</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+++</td>
<td>+++</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Ti</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+++</td>
<td>+</td>
<td>+++</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Fe</td>
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<td>+++</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+++</td>
</tr>
<tr>
<td>Ta</td>
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<td>-</td>
<td>-</td>
<td>+</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cd</td>
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<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

The Table shows the strength of interference for the wavelengths of Cd and Pb when 1000 mg/kg of the corresponding matrix elements are introduced

+ no or small interference (typical less than 0.05 mg/kg)
++ medium interference (typical between 0.05 mg/kg and 0.2 mg/kg)
+++ strong interference (typical more than 0.2 mg/kg)
Background correction

In the case of changing background by the main matrix of solution and affecting the emission intensities ($I_x$), the emission intensities should be obtained by deducting the background intensities ($I'_x$). Figure 7 shows one example of the effect of background correction. Figure 7(a) shows the example of uniform background versus wavelength. In this case, background could be corrected by both of position A and B. Figure 7(b) shows the example of changing background versus wavelength. In this case, background intensities should be corrected by obtaining the background intensities ($I'_x$), which are calculated by both position A and position B of emission intensities.

![Figure 7: Background Correction](image)

Depending on the equipment, alternatively standard addition may be used (instead of background correction).

13.7.2 ICP-MS

If a stable isotope is found, mass/charge number of a number of 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 19: Examples for mass-charge-ratios

<table>
<thead>
<tr>
<th>Element</th>
<th>Isotope</th>
<th>Isobar</th>
<th>Polyatomic ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>111Cd</td>
<td></td>
<td>MoO, MoOH, ZrOH</td>
</tr>
<tr>
<td></td>
<td>112Cd</td>
<td>Sn</td>
<td>MoO, MoOH</td>
</tr>
<tr>
<td></td>
<td>113Cd</td>
<td>In</td>
<td>MoO, MoOH, ZrOH, RuO</td>
</tr>
<tr>
<td></td>
<td>114Cd</td>
<td>Sn</td>
<td>MoO, MoOH, RuO</td>
</tr>
<tr>
<td>Pb</td>
<td>204Pb</td>
<td></td>
<td>PtO</td>
</tr>
<tr>
<td></td>
<td>206Pb</td>
<td></td>
<td>IrO</td>
</tr>
<tr>
<td></td>
<td>207Pb</td>
<td></td>
<td>PtO</td>
</tr>
<tr>
<td></td>
<td>208Pb</td>
<td></td>
<td>PtO</td>
</tr>
</tbody>
</table>

### 13.7.3 AAS

Recommended measurement wavelengths for AAS

#### Table 20: Examples for wavelengths for AAS

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength /nm</th>
<th>Slit width / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>228.8</td>
<td>0.7</td>
</tr>
<tr>
<td>Pb</td>
<td>261.4</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>217.0</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>283.3</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Gas type: Acetylene/Air

Light source: Electrodeless discharge lamp or hollow cathode lamp
A Practical Guide for Testing Electronic Products

A.1 Introduction

The purpose of this Appendix is to provide practical guidance for performing testing of regulated substances in electronic products. Such guidance is important, since there are many practical challenges associated with testing a complete electronic product. Two significant challenges include:

- Obtaining a representative sample
- Applying legal threshold requirements

A typical electronic product is made up of hundreds of individual components such as integrated circuits (ICs), discrete components (resisters, capacitors, diodes, etc), wires, cables, printed circuit boards, connectors, fasteners, sensors, etc. Each of these components, in turn, has a unique mix of materials that makes up its composition. For example, an integrated circuit alone may consist of a silicon die, die attach material, epoxy underfill, mold compound, leads, and lead plating materials. These materials are often heterogeneous, made up of a set of materials themselves. Obtaining a representative sample of the device for testing purposes can be a daunting challenge.

To complicate matters, acceptable legal thresholds for cadmium, hexavalent chromium, lead, mercury, PBBs and PBDEs are not uniformly defined in all geographies where such laws exist. In addition, some regulated substance thresholds have been set at the “homogeneous material” level, making testing of a typical finished electronic product impossible from a practical standpoint. Moreover, exemptions may exist for certain technical applications that use the regulated substances. So, products may contain regulated materials in exempt applications and still be in compliance with the legal restrictions. Finally, some companies have chosen to go beyond legal requirements and set more conservative thresholds for business and/or risk management reasons.

To address this challenge, it is recommended to focus testing on select “high risk” areas of the product that can be performed within a reasonable time frame and within a reasonable cost budget. What follows is a practical method for assessing the presence of regulated substances in electronic products using the test methods identified in this standard.

A.2 Scope

Annex A provides practical guidance and examples for the testing of electrotechnical products. The annex includes examples and a dedicated section discussing interpretation of test results on the basis of choices made during sample selection and preparation. Examples and values are provided for guidance only. It is not within the scope of this standard to provide information on regulations, which change with time. The user is advised to remain informed about applicable maximum limits and exemptions to the limits by checking pertinent, existing regulations. Moreover, due to the vast number and diverse nature of electronic products, it is not possible to cover all electronic products in detail in this Appendix. If detailed guidance is needed by product type or product family, such guidance should be developed by those relevant product Technical Committees (TCs) within IEC.

A.3 Testing of Products

Testing of products can be performed at a variety of levels. For purposes of this Appendix, guidance for evaluating a product will be grouped into 3 categories:
- Evaluation without disassembly
- Evaluation with simple disassembly
- Evaluation with detailed disassembly

Figure A-1 below illustrates the various levels of evaluation.

![Evaluation Levels for Testing](image)

**Figure A-1: Evaluation Levels for Testing**

### A.3.1 Evaluation of a Product without Disassembly

A product may be evaluated for the presence of regulated substances without disassembly. Such evaluation may be very limited, dependent on the product in question. In most cases, external components or materials such as external cases, cables, cords, screws, or fasteners can be evaluated without disassembly. External parts may often be evaluated using the screening methods defined in clause 6 of this standard.

Table A-1 lists common uses of regulated substances in select external parts. The table is not exhaustive, but provides a good starting point for screening external parts. Most uses of restrictive substances have historically fallen into one of these applications.
<table>
<thead>
<tr>
<th>External Part</th>
<th>Regulated Substance</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plastic enclosures, fasteners,</td>
<td>Lead</td>
<td>Additive to plastic</td>
</tr>
<tr>
<td>clips, screws, etc.</td>
<td>Cadmium</td>
<td>Additive to plastic; plastic colorant</td>
</tr>
<tr>
<td>PBDEs</td>
<td>Good retardant</td>
<td></td>
</tr>
<tr>
<td>Glass and ceramics</td>
<td>Lead</td>
<td>Additive to glass</td>
</tr>
<tr>
<td>Metal enclosures, fasteners,</td>
<td>Hexavalent Chromium</td>
<td>Plating surface treatment; conversion</td>
</tr>
<tr>
<td>clips, screws, etc.</td>
<td></td>
<td>coating</td>
</tr>
<tr>
<td>Cables, cords, wires</td>
<td>Lead</td>
<td>Additive to plastic; stabilizer</td>
</tr>
<tr>
<td>Decorative name plates, buttons,</td>
<td>Mercury</td>
<td>Additive to certain plastics; curing</td>
</tr>
<tr>
<td>etc</td>
<td></td>
<td>agent</td>
</tr>
</tbody>
</table>

Advantages of evaluation without disassembly are:

- Relatively quick and simple evaluation
- Many historical uses of regulated substances occurred in external parts, particularly cadmium.

Disadvantages of evaluation without disassembly are:

- Cannot evaluate internal parts which may contain regulated substances

A.3.2 Evaluation of a Product Using Simple Disassembly Techniques

In order to evaluate the internal components of an electronic product, some level of disassembly is required. For many products, simple disassembly techniques may be used to disassemble an electronic product for further testing.

At a minimum, most electronic products contain the following two elements:

- Housing – outer housing protects the inner workings of the electronic product and may provide safety, functional, cosmetic and other benefits. Plastics and metals are typically used for this purpose.
- Printed circuit board assemblies – printed circuit board to which is attached many electronic components (ICs, capacitors, resistors, diodes, etc). Some products contain multiple printed circuit board assemblies.

In addition, many electronic products contain a variety of additional internal parts and components. A few examples include:

- power supplies
- capacitors, voltage regulators, converters
- storage and memory devices
- cooling mechanisms
- amplifiers, speakers, microphones
- batteries
- numerous other electrical and mechanical parts

It is impossible to list all categories of internal parts for all electronic products. If such a detailed list is required, it should be developed by those industry sectors that manufacture each product type.
A.3.2.1 Disassembly Steps

The following general guidance can be used in simple disassembly of an electronic product.

For many electronic products, internal parts may be accessed by removal of the housing around the product. For some products, this can be accomplished using simple tools such as a screwdriver. Other products require specialized tools. Specialized tools are often required for products that limit the consumer’s access due to safety concerns (e.g. exposure to hazardous energies).

A.3.2.2 Testing

Once the housing material has been removed, access is generally available to many internal parts of the product. At this point, testing of the internal parts may be performed using the test methods outlined in clause 6 to 13 of this standard and illustrated in Figure 1 of this standard.

Table A-2 lists common uses of regulated substances in select internal parts. The table is not exhaustive, but provides a good starting point for screening common internal parts. Most uses of restrictive substances in internal parts have historically fallen into one of these applications.

Advantages of evaluation with simple disassembly are:

- Provides more thorough evaluation of the product
- Can often be accomplished without significant costs or time commitment, if focus is limited to “high risk” components.

The primary disadvantage of evaluation with simple disassembly is:

- May not allow assessment of all homogeneous materials

Table A-2: Use of Regulated Substances in Common Internal Parts

<table>
<thead>
<tr>
<th>Internal Part</th>
<th>Regulated Substance</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plastic parts, housings, fasteners, clips, screws, etc.</td>
<td>Lead</td>
<td>Additive to plastic</td>
</tr>
<tr>
<td>Glass and ceramic parts such as resistors, diodes, etc.</td>
<td>Lead</td>
<td>Additive to glass</td>
</tr>
<tr>
<td>Glass and ceramic parts such as resistors, diodes, etc.</td>
<td>Cadmium</td>
<td>Additive to plastic; plastic colorant</td>
</tr>
<tr>
<td>Glass and ceramic parts such as resistors, diodes, etc.</td>
<td>PBDEs</td>
<td>Flame retardant</td>
</tr>
<tr>
<td>Metal fasteners, clips, screws, etc</td>
<td>Hexavalent Chromium</td>
<td>Plating surface treatment; conversion coating</td>
</tr>
<tr>
<td>Cables, cords, wires</td>
<td>Lead</td>
<td>Additive to plastic; stabilizer</td>
</tr>
<tr>
<td>Cables, cords, wires</td>
<td>Cadmium</td>
<td>Additive to plastic; stabilizer</td>
</tr>
<tr>
<td>Printed circuit boards</td>
<td>Lead</td>
<td>Solder, finishes</td>
</tr>
<tr>
<td>Printed circuit boards</td>
<td>PBDE</td>
<td>Flame retardant</td>
</tr>
<tr>
<td>Electrical components</td>
<td>Lead</td>
<td>Solder on terminal finishes</td>
</tr>
<tr>
<td>Inks</td>
<td>Lead</td>
<td>Additive</td>
</tr>
<tr>
<td>Inks</td>
<td>Cadmium</td>
<td>Additive</td>
</tr>
<tr>
<td>Inks</td>
<td>Hexavalent Chromium</td>
<td>Additive</td>
</tr>
<tr>
<td>Switches, relays</td>
<td>Mercury</td>
<td>Component of switch/relay</td>
</tr>
<tr>
<td>Bulbs</td>
<td>Mercury</td>
<td>Used in fluorescent bulbs</td>
</tr>
</tbody>
</table>
### A.3.3 Evaluation of a Product Using Detailed Disassembly Techniques

In most cases, detailed disassembly and testing of a complete electronic product will require destruction of the product and may require hundreds or even thousands of analytical tests. As a result, such detailed disassembly should be limited where possible. If required, detailed disassembly should focus on parts with highest risk of containing regulated substances (see Tables A-1 and A-2).

It should be noted that when testing for certain regulated substances, detailed disassembly may not be necessary to answer certain questions. For example, an analyst needs to know whether lead has been used in any components of a printed circuit board. One of the most common uses of lead in electronics is the solder used to attach components to a board. Although relatively small amounts of solder are used (3 g to 5 g per board), the lead content of the solder is high enough that the overall lead content of the entire board is substantial. As a result, it may not necessary to disassemble the printed circuit board item-by-item to test only the solder material. It may be faster and less expensive to grind and homogenize the entire circuit board and analyze the resulting powder.

To illustrate this point, consider the data in Table A-3 obtained by the High Density Packaging User Group (HDPUG Design for Environment Phase I Report, Feb. 2003). The study evaluated the lead content of entire printed circuit boards and whole integrated circuits using destructive sample preparation procedures similar to those in clause 5 of this standard and elemental analysis test methods similar to those in clauses 11 through 13 of this standard. If used, lead consistently appeared in concentrations far exceeding anticipated future regulatory limits. If the user finds it sufficient to know that lead is used in the board or integrated circuit, the destructive test suffices.

It should be noted that additional testing may be required in the following situations: 1) the user requires knowledge of the exact locations of Pb-containing materials, and 2) the test result for total lead indicated a concentration below the regulatory limit. In both cases, further testing may be needed. In the first case, the existence of numerous exemptions to regulations allowing the use of lead in certain materials, viz. ceramics and copper alloys, may mean that only a fraction of the total lead on the board is present in a regulated material such as solder. Indeed, it may be that all lead on the board is present in exempt materials. In that event, the user shall employ procedures to isolate the various lead-containing materials and test them individually. In the second case, if the amount of solder is low and no other sources of lead are present, the total lead result for the entire board will be low, even though the board contains lead solder, which is regulated.

See A.5 for additional discussion of interpretation of test results.

<table>
<thead>
<tr>
<th>Part</th>
<th>Average Lead Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Network interface card</td>
<td>10,000 mg/kg</td>
</tr>
<tr>
<td>PC motherboard</td>
<td>28,000 mg/kg</td>
</tr>
<tr>
<td>Telecommunications board</td>
<td>37,000 mg/kg</td>
</tr>
<tr>
<td>Integrated circuit</td>
<td>10,000 mg/kg</td>
</tr>
</tbody>
</table>

### A.4 Additional Guidance

This clause provides additional guidance for testing based on the experience of the IEC TC111 WG3. The tables that follow may help reduce unnecessary testing and further focus the testing toward “high risk” areas of the electronic product under evaluation.
Table A-4: Historical Use of Regulated Substances in Plastic Colorants

<table>
<thead>
<tr>
<th>Colorant</th>
<th>Regulated Substance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brightly colored plastics:</td>
<td></td>
</tr>
<tr>
<td>Yellow</td>
<td>Cadmium, lead and chromium VI (as lead chromate)</td>
</tr>
<tr>
<td>Orange</td>
<td></td>
</tr>
<tr>
<td>Red</td>
<td></td>
</tr>
<tr>
<td>Green</td>
<td></td>
</tr>
</tbody>
</table>

Table A-5: Historical Use of PBB/PBDE in Plastic Resins

<table>
<thead>
<tr>
<th>Plastic Resin</th>
<th>Compatible with PBB/PBDE?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene (PS)</td>
<td>Yes</td>
</tr>
<tr>
<td>High-impact Polystyrene (HIPS)</td>
<td>Yes</td>
</tr>
<tr>
<td>Acrylonitrile/Butadiene/Styrene (ABS)</td>
<td>Yes</td>
</tr>
<tr>
<td>Modified Polyphenylene Ether (PPE)</td>
<td>No</td>
</tr>
<tr>
<td>Polycarbonate (PC)</td>
<td>No</td>
</tr>
<tr>
<td>PC/ABS</td>
<td>No</td>
</tr>
</tbody>
</table>

A.5 Interpretation of Test Results Applied to Materials Isolated from Products

After product materials have been isolated for testing and the selected test methods applied, test results shall be interpreted carefully with regards to compliance with the applicable standards. It is possible that materials isolated from products contain a composite mixture of several homogeneous materials in unknown proportions. An example of such a composite would be a PCB component such as a resistor which has been ground into a powder for analysis. Another example is use of a portable XRF analyzer to test PCB components, when the XRF measurement is an analysis of multiple homogeneous materials in the component.

It is not possible to interpret a test result for a particular substance in terms of the concentration in the original homogeneous material unless the weight proportion of the specific homogeneous material in the test sample is known, and it is certain that this is the sole source of the substance of interest. This information may be difficult to determine for a composite sample isolated from finished products. However, test results from composite samples can possibly be used for rough screening analysis if there is adequate mass of a suspect homogeneous material in the test sample to generate a minimum detection of a regulated substance using the selected test method. If detailed information is available regarding the application of the regulated substance in a homogeneous material in a particular composite sample, it may also be possible to back-calculate a substance screening level which would give information on whether further compliance testing is necessary. This would need to be done for each type of composite sample. Lacking this information, it may not be possible to reliably interpret numerical test results from materials isolated from products with regards to compliance levels of regulated substances. Three examples for this are given below:

- Result for theoretical composite sample A: No detections of regulated substances. Caution with interpretation: Although no regulated substances were detected using the selected test method, there may not have been adequate mass of a non-compliant homogeneous material in the composite sample to reach the minimum detection level for a regulated substance of interest using the selected test method. This could happen with a very small mass of homogenous material such as a coating. Therefore it is uncertain if regulatory compliance requirements are satisfied in this sample.
- Result for theoretical composite sample B: 250 mg/kg lead. Caution with interpretation: Although a numerical result for a detected regulated substance was obtained, it cannot be
related back to the concentration of the substance in the original homogeneous material unless the weight proportion of the specific homogeneous material in the test sample is known, and it is certain that this is the sole source of the substance of interest. Therefore it is uncertain if the regulatory compliance requirement of 1000 mg/kg for is satisfied in this sample.

- Result for theoretical composite sample C: 1500 mg/kg lead. Caution with interpretation: Although a numerical result for a detected regulated substance was obtained above the regulatory threshold, it is possible the source of lead could be from an application exempted by the applicable regulations. Therefore it is uncertain if the regulatory compliance requirement has been exceeded in this sample without further investigation.
Annex B
(Informative)

Bibliography


e) California Electronic Waste Recycling Act of 2003 (S.B. 20)

f) California Electronic Waste, Advanced Disposal Fees (S.B. 50)

g) California Environmental Protection Agency, Procedural SOP No. 914-S, Preparation of Cold Cathode Fluorescent Lamps for Mercury Testing, including WET and TCLP, Department of Toxic Substances Control Revision No. 2, 2004.

h) Certificate of analysis/documentations: Wellington laboratory, Southgate Dr. Guelph ON Canada.


o) EPA 1613: 1994: Tetra- through octa-chlorinated dioxins and furans by isotope dilution HRGC/HRMS.


s) EPA method 3050B:1996 Rev. 2 Acid digestion of sediments, sludges and soils

t) EPA method 3052:1996 Microwave assisted acid digestion of siliceous and organically based matrices.


v) EPA method 6010B:1996 Rev 2 Inductively coupled plasma-atomic spectrometry


y) EPA SW-846 Method 3050B, Acid digestion of sediments, sludges and soils

z) EPA SW-846 Method 3052, Microwave assisted acid digestion of siliceous and organically based matrices

aa) EPA SW-846 Method 6010B, Inductively coupled plasma-atomic emission spectrometry

bb) EPA SW-846 Method 7000, Series measurement methods for lead, cadmium, chromium, & mercury

c) EPA SW-846 Method 7470A, Mercury in liquid waste (manual cold-vapor technique)

d) EPA SW-846 Method 7471A, Mercury in solid of semisolid waste (manual cold-vapor technique)

e) EPA SW-846 Method 7474, Mercury in sediment and tissue samples by atomic fluorescence spectrometry


gg) GMW3034 “Absence of Hexavalent Chrome (VI) Coatings”


ll) Management Methods on the Prevention and Control of Pollution Caused by Electronic information Products


oo) Reference and handling guide (GC-MS characterization and analysis of selected halogenated aromatic compounds): Wellington laboratory, Southgate Dr. Guelph ON Canada.


vv) ZVO-0102-QUA-02 “Qualitative Analysis of Cr-VI in Passivation Layers on Parts by Spot Analysis”
Commercially Available Certified Reference Materials (CRM)

A variety of commercially available reference materials exist, mainly polymers and metals, but also, in glass and ceramic. These materials have been specially formulated (doped) with the five substances (Pb, Cd, Hg, Cr and Br), possibly with other substances as well. These doped materials were then analyzed using a variety of wet chemistry methods at a number of testing laboratories to determine the concentration of these elements. Table C-1 gives an overview over existing CRMs suited for regulated substances in electrotechnical products.

Table C-1: CRMs suitable for regulated substances

<table>
<thead>
<tr>
<th>Substance</th>
<th>CRM</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBBs / PBDEs</td>
<td>NMIJ-8108-a</td>
<td>PS with DecaBDE (325 mg/kg), Disk type&lt;br&gt;BM: Round robin test (final report available): ABS, PS with OctaBDE; PUR foam, epoxy resin with PentaBDE</td>
</tr>
<tr>
<td>Total Br</td>
<td>ERM-EC680, ERM-EC681</td>
<td>Plastics packaging and packaging material: certification of mass fractions of As, Br, Cd, Cr, Hg, Pb and S in polyethylene</td>
</tr>
<tr>
<td>Cr VI</td>
<td>BAM-S004</td>
<td>Glass for cosmetics; certification of mass fractions of hexavalent chromium and of total chromium in glass</td>
</tr>
<tr>
<td>Total Cr</td>
<td>ERM-EC680, ERM-EC681&lt;br&gt;BAM-S004&lt;br&gt;NMIJ 8112-a, 8113-a&lt;br&gt;NMIJ 8115-a, 8116-a</td>
<td>See above (Comment, Total Br)&lt;br&gt;See above (Comment, Cr VI)&lt;br&gt;ABS with certification of mass fractions of Cd, Cr, Hg, Pb, Pellet type&lt;br&gt;ABS with certification of mass fractions of Cd, Cr, Hg, Pb, Disk type</td>
</tr>
<tr>
<td>Hg</td>
<td>ERM-EC680, ERM-EC681&lt;br&gt;NMIJ 8112-a, 8113-a&lt;br&gt;NMIJ 8115-a, 8116-a</td>
<td>See above (Comment, Total Br)&lt;br&gt;See Above (Comment, Total Cr)</td>
</tr>
<tr>
<td>Pb</td>
<td>ERM-EC680, ERM-EC681&lt;br&gt;BCR-126A&lt;br&gt;BCR-691&lt;br&gt;BCR-355&lt;br&gt;BCR-326, BCR-327, ERM-EB325&lt;br&gt;SRM 127b&lt;br&gt;SRM 1129&lt;br&gt;SRM 1131&lt;br&gt;NMIJ 8112-a, 8113-a&lt;br&gt;NMIJ 8115-a, 8116-a</td>
<td>See above (Comment, Total Br)&lt;br&gt;Certification of a lead glass&lt;br&gt;Pb in bronze discs&lt;br&gt;Cd + Pb in ZnAl4&lt;br&gt;Cd + Pb in Zn&lt;br&gt;Solder 40Sn-60Pb (powder)&lt;br&gt;Solder 63Sn-37Pb (disk)&lt;br&gt;Solder 60Pb-40Sn (disk)&lt;br&gt;See Above (Comment, Total Cr)</td>
</tr>
<tr>
<td>Cd</td>
<td>ERM-EC680, ERM-EC681&lt;br&gt;VDA-001 to VDA-004&lt;br&gt;BCR-355&lt;br&gt;BCR-326, BCR-327, ERM-EB325&lt;br&gt;NMIJ 8112-a, 8113-a&lt;br&gt;NMIJ 8115-a, 8116-a</td>
<td>See above (Comment, Total Br)&lt;br&gt;Association of German Automobile Manufacturers; Certification for cadmium in polyethylene&lt;br&gt;Cd + Pb in ZnAl4&lt;br&gt;Cd + Pb in Zn&lt;br&gt;See Above (Comment, Total Cr)</td>
</tr>
</tbody>
</table>