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Title:  
IEC 62321, Ed.1: Procedures for the Determination of Levels of Regulated Substances in Electrotechnical Products

(Titre) :

Introductory note

Global legislation dealing with hazardous substances, most notably the Directive on "Restriction of Hazardous Substances" (RoHS) in Europe, is forcing the electrotechnical industry to develop methods for analytical testing of its components and products for regulated substances. Recognizing the electrotechnical industry's need to develop global, standardized test methods for regulated substances in electrical, electronic and electrotechnical products, ACEA (IEC's Advisory Committee on Environmental Aspects) decided in March 2004 to form an *ad hoc* working group to develop test procedures that will allow the electrotechnical industry to determine the levels of six regulated substances (Pb, Hg, Cd, Cr VI, PBB, PBDE) in electrotechnical products on a consistent global basis.

Through AC/19A/2004 experts for this ad hoc WG were nominated and a first working draft was finished by the ad hoc WG in December 2004. This draft was also included in the NP (111/2/NP) for TC 111, drawing comments by NCs as well as by industry stakeholders. The work started in the ACEA ad hoc WG was in March 2005 successfully transferred to TC 111/WG 3 (111/9/RVN), officially established in the first IEC TC 111 meeting (Milano, 2005-03-22/23) with the goal to publish a CD by June 2005 (see Decision 01/03 in 111/11/INF). The WG 3 is under severe time pressure, as the EU RoHS directive will come into force 1<sup>st</sup> July 2006 and there is a very strong market requirement to provide a standard by then.

The CD addresses the comments received by the NCs (from 111/9/RVN), other stakeholders and the results of the first TC 111/WG3 meeting, held in Paris on 2005-05-23/24 (111/20/INF). To understand how the comments have been addressed, an additional document has been prepared: 111/25/INF, which lists all comments received and the action taken by the WG 3.

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# International Electrotechnical Commission

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**Procedures for the Determination of Levels of  
Six Regulated Substances (Lead, Mercury,  
Hexavalent Chromium, Polybrominated  
Biphenyls, Polybrominated Biphenyl Ether) 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 Biphenyl Ether) in Electrotechnical Products**

### **FOREWORD**

- 1) The IEC (International Electrotechnical Commission) is a worldwide organization for standardization comprising all national electrotechnical committees (IEC National Committees). The object of the IEC is to promote international co-operation on all questions concerning standardization in the electrical and electronic fields. To this end and in addition to other activities, the IEC publishes International Standards. Their preparation is entrusted to technical committees; any IEC National Committee interested in the subject dealt with may participate in this preparatory work. International, governmental and non-governmental organizations liaising with the IEC also participate in this preparation. The IEC collaborates closely with the International Organization for Standardization (ISO) in accordance with conditions determined by agreement between the two organizations.
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International Standard IEC XXX has been prepared by WG 3: Procedures for the Determination of Levels of Regulated Substances in Electrotechnical Products, of IEC technical committee 111: Environment.



## 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 substance like Lead (Pb), Mercury (Hg), Cadmium (Cd), Hexavalent Chromium (Cr VI), and some types of brominated flame retardants (like Polybrominated Biphenyls, PBB, Polybrominated Diphenyl Ethers, PBDE) in electrotechnical products is regulated in current and proposed legislation e.g. in:

- European Union (EU) directive on the “Reduction of certain Hazardous Substances in electrical and electronic equipment” (RoHS)
- Chinese draft legislation on “Management Methods on the Prevention and Control of Pollution Caused by Electronic information Products”
- US (California) Electronic Waste Recycling Act of 2003 (S.B. 20) and Electronic Waste, Advanced Disposal Fees (S.B. 50)

The EU RoHS directive prohibits Lead (Pb), Mercury (Hg), Cadmium (Cd), Hexavalent Chromium (Cr VI), and two types of brominated flame retardants, Polybrominated Biphenyls (PBB) and Polybrominated Diphenyl Ethers (PBDE) from being used in electronic and electrical equipment (EEE) from 1st July 2006. The same substances are regulated in the Chinese draft legislation, adhering to the same timeline as the EU RoHS. Likewise, California restricts the same substances on the same timeline, although for a narrower set of products than the EU RoHS.

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 normative document is therefore to provide test procedures that will allow the electrotechnical industry to determine the levels of the regulated substances Pb, Hg, Cd, Cr VI, PBB, PBDE (EU RoHS, China, US, Japan, etc.) in electrotechnical products on a consistent global basis.

# **Procedures for the Determination of Levels of Six Regulated Substances (Lead, Mercury, Hexavalent Chromium, Polybrominated Biphenyls, Polybrominated Biphenyl Ether) 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 two types of brominated flame retardants, Polybrominated Biphenyls (PBB) and Polybrominated Diphenyl Ethers (PBDE) contained in electrotechnical products.

Examples of categories of electrotechnical products are:

- Large household appliances
- Small household appliances
- IT and telecommunications equipment
- Consumer equipment
- Lighting equipment
- Electrical and electronic tools (with the exception of large-scale stationary industrial tools)
- Toys, leisure and sports equipment
- Automatic dispensers

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**

- a) Reduction of certain Hazardous Substances in electrical and electronic equipment (RoHS)
- b) Management Methods on the Prevention and Control of Pollution Caused by Electronic information Products
- c) US (California) Electronic Waste Recycling Act of 2003 (S.B. 20)
- d) US (California) Electronic Waste, Advanced Disposal Fees (S.B. 50)
- e) Other references are found in the reference sections of the test procedures

## **3 Definitions**

For the purpose of this document, the following terms and definitions apply. Other terms and definitions are found in the terms and definition sections of the test procedures.

### **3.1**

#### **Electrotechnical Products**

Products which are dependent on electric currents or electromagnetic fields in order to work properly and equipment for the generation, transfer and measurement of such currents and fields and designed for use with a voltage rating not exceeding 1 000 volts for alternating current and 1 500 volts for direct current.

### 3.2

#### **Field Replaceable Unit**

Part, component or subassembly that is easily removed (mechanically disjointed) using ordinary tools.

NOTE “Easily removed” consists of using ordinary tools to perform such functions as screwing or disconnecting, and only without irreversibly destroying the unit.

### 3.3

#### **Substance**

Substances are chemical elements and their compounds (e.g. lead is a chemical element and lead oxide is a compound). Registry numbers of the Chemical Abstracts System of the American Chemical Society (CAS #) are attributed to all chemical elements and most of their compounds and should be used for identification purposes.

### 3.4

#### **Screening**

An analytical approach with the primary goal to quantify the concentration of an element of interest (analyte) in tested material.

### 3.5

#### **Polymer Materials**

A range of synthetic or semi-synthetic organic condensation or polymerization products that can be molded or extruded into objects or films or fibers.

NOTE: Examples of polymer materials are polyethylene, polyvinyl chloride, epoxy resin, polyamide, polycarbonate ABS resin, polystyrene, etc.

### 3.6

#### **Metallic Materials**

Metallic materials are combinations of metallic elements. Metallic materials include all ferrous, non-ferrous and alloy materials.

NOTE: Examples of metallic materials are Fe-alloys, Ni-alloys, Sn-alloys, Al-alloys, mg-alloys, Cu-alloys, Zn-alloys, precious metals alloys etc.

### 3.7

#### **Electronics**

An element of an electromechanical product which unto itself does not form an electrical system. They are sometimes called electronic components, electronic parts, or piece parts.

NOTE: Examples of electronics are semiconductors, active components like diodes and integrated circuits, passive components like resistors and capacitors, electrical and electronic connectors, wound components, relays, printed circuit boards (PCB, also known as printed wiring board, PWB) etc.

### 3.8

#### **Analyte**

Substance or element tested for.

### 3.9

#### **Matrix**

The material or substance, form or state in which the analyte is embedded.

Other terms and definitions are found in the terms and definition sections of the test procedures.

## **4 Test Procedure Overview**

### **4.1 Test Procedure Scope**

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

- Analytical test procedures
- Laboratory implementation

Analytical test procedures have to be 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 step can itself be divided into seven important points:

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

The first point includes the scope of the method, the preferred application and a short summary of the method. It also highlights the opportunities for the best use of the test procedure and also the risks due to the inherent limitations of the procedure. The second important point is also how the method becomes traceable to commercial reference standards and suitable calibration samples. The third point will define the terms used throughout the method procedure. The fourth point describes the apparatus and the needed equipment and materials used for the method. The fifth point describes all the reagents used when measuring using the described method procedure. The sixth important covers the sample preparation for the samples themselves. The seventh point covers the actual test procedure related to the analytical instrument used. It describes the instrument performance, the sample analysis as well as the calculation of the analytical results. Content of the test report will also be summarized. This point also covers the quality aspects directly related to the chosen analytical test procedure.

Individual test procedure descriptions in chapters 6 to 15 follow this seven point outline.

The laboratory implementation will not be covered in this document, as labs should be 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. IEC/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 following below to determine the levels of the six regulated substances. A sample can either be a polymer material, a metallic material or electronics (e.g. in form of populated PWBs or components).

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

The entity can thus decide to prepare a sample which is a “homogenous material” according to the EU guidance. For this kind of sample the procedures offered for metallic materials or polymer materials are especially suited.

NOTE: The EU Technical Advisory Committee (TAC) 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, 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 can also decide to prepare a sample which is on the component level. For this kind of sample the procedures offered for electronics are especially suited.

NOTE: Components can be described as smallest parts of electrical or electronic equipment that can be separated from the equipment by using ordinary tools without destroying the function of the part. Examples include electronic parts like unpopulated printed circuit boards, resistors, capacitors, diodes, integrated circuits; electromechanical parts like molded connectors, cable insulation; or mechanical parts like screws, housings or cabinets (with a surface treatment, e.g. plated, coated and/or painted), keys (from a keyboard), decorated/coated glass, glass-ceramics components, etc.

The entity can also decide to prepare a sample which is on the field replaceable unit (FRU) level. For this kind of sample the procedures offered for electronics are especially suited.

NOTE: A FRU is a part, component or subassembly that is easily removed (mechanically disjointed) using ordinary tools. Examples of the field replaceable units in a desktop personal computer (PC) may include housing, printed wiring assembly (motherboard), chassis, display, cables, batteries, key board, mouse, fan, drives (CD-ROM, DVD), power supplies, add-in cards, etc.

The procedure to obtain the sample is also outside of the scope of this document. Guidance on how to obtain a sample is however given in Annex A.

### 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.

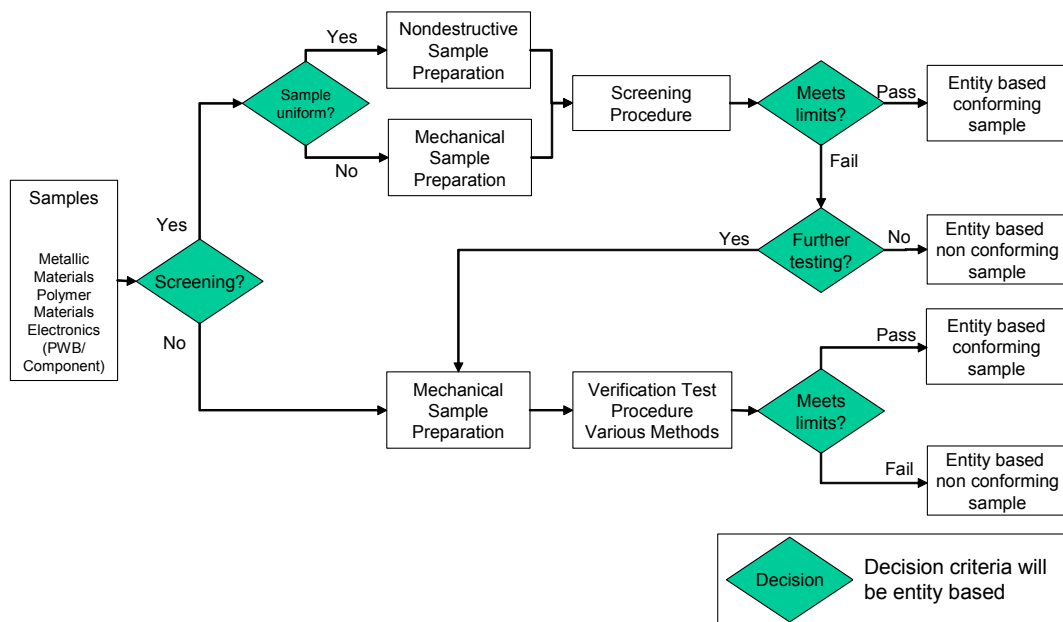


Figure 1: Flowchart of the Test Procedure

After obtaining the sample, which can either be a polymer material, a metallic material or electronics (e.g. in form of populated PWBs or components), a decision has to be taken, whether the screening test procedure or the verification test procedure using a variety of test methods should be used.

The screening test procedure can 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 must be made by judging the uniformity of the sample. A screening of representative samples of many uniform materials (such as plastics, alloys, glass) can be done non-destructively, while for other, more complex samples (like a populated printed wiring board) 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 chapter 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 chapter 6. It must 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.

Screening analysis allows one to distinguish between samples in three basic classifications:

- Pass (white area): Samples that clearly contain concentrations, which are below the tolerated values
- Fail (black area): Samples that are clearly higher than the tolerated values
- Inconclusive (grey area): Samples that require additional investigation, due to inconclusive analysis results

The verification test procedure is performed after a mechanical sample preparation using a variety of analytical procedures tailored to the regulated substances and the material of the sample, which can be either polymer materials, metallic materials or electronics (in form of populated PWBs or components). Table 1 gives an overview of the verification methods, which are described in detail in chapter 7 to 14. 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**

Steps	Substances	Polymer Materials	Metal Materials	Electronics (PWBs/Components)
Mechanical sample preparation (Chapter 5)		Direct measurement Grinding	Direct measurement Grinding	Grinding
Chemical sample preparation		Microwave digestion Acid digestion Dry Ashing Solvent extraction	Acid digestion	Microwave digestion Acid digestion Solvent extraction
Analytical technique definition (incl. typical margins of errors)	PBB/PBDE	GC/MS (Chapter 7) HPLC/UV (Chapter 8)	NA	GC/MS (Chapter 7) HPLC/UV (Chapter 8)
	Cr VI	Alkaline Digestion/ Colorimetric Method (Chapter 10)	Spot-test procedure/ boiling-water-extraction procedure (Chapter 9)	Alkaline Digestion/ Colorimetric Method (Chapter 10)
	Hg	ICP-AES, ICP-MS, CV AAS, AFS (Chapter 11)		

	Pb/Cd	ICP-AES, ICP-MS, AAS (Chapter 12)	ICP-AES, ICP-MS, AAS (Chapter 13)	ICP-AES, ICP-MS, AAS (Chapter 14)
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After the verification test procedure it can be decided if the sample meets the limits based on the entity's criteria for regulated substances.

#### 4.4 Adjustment to Material (Matrix)

Analytical procedures for regulated 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 have to 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 polymer materials, mostly technical polymers with a whole series of additives that can moreover be painted; metallic materials as well as alloys of different types; and electronics such as (populated) printed wiring boards (PWBs) and electrical and electronic components.

#### 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 the way for arriving at the sample
- e) A reference to this IEC standard, the used procedure (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) Results from all quality assurance and quality control (QA/QC) tests, including results from blank test, and a list of reference materials used and their origin
- i) 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

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 sections 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 document describes the procedure for the mechanical sample preparation of electrotechnical products. 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 sections describe common mechanical particle size reduction technique. Selection of the appropriate technique(s) is dependent on the required particle size for the test procedure to be employed.

The reduction shall be implemented without introducing or contaminating the final sample with elements of interest from the process itself or compromising the sample to effect loss of elements of interest (e.g. volatilization due to heat). The laboratory shall be able to demonstrate by experiment that the procedure employed for mechanical sample preparation do not directly contribute detectable amounts of interest elements or compromise the specimen to effect loss of those elements. The laboratory shall 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 References, Normative References, Reference Methods and Reference Materials

- a) EN 13346:2000 Characterization of sludges – Determination of trace elements and phosphorus – Aqua regia extraction methods
- b) EPA method 3052:1996 Microwave assisted acid digestion of siliceous and organically based matrices.
- c) EPA method 3050B:1996 Rev. 2 Acid digestion of sediments, sludges and soils
- d) ASTM D 4004-93:2002-Total digestion with alkali fusion
- e) EN 1122:2001 Plastics – Determination of cadmium – Wet decomposition method
- f) ISO 247: 1990: Rubber – Determination of ash
- g) ISO 3696: 1987 – water specification
- h) ISO 40 and JIS 40 – specification of hydrofluoric acid

### 5.3 Terms and Definitions

- a) n.a.

### 5.4 Apparatus / Equipment and Materials

- a) Course Grinding or Cutting mill with 4 and 1 mm or similar stainless steel bottom sieve
- b) Centrifugal mill with 25µm tungsten carbide (WC) coated steel sieve, 6-fold WC coated rotor, (for uniform plastic material a 1mm steel sieve is appropriate). In order to avoid any risks of impurities during milling a 1 mm titan sieve and a steel/titan 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) 250ml Glass Beaker
- j) Liquid Nitrogen (N<sub>2</sub>)

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

## **5.5 Procedure**

### **5.5.1 Sample**

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

### **5.5.2 Manual Cutting**

Suitable for rough cutting and preparation of samples for further reduction. Samples are precut to a size of no more than 2×10×10 cm<sup>3</sup>.

- a) Electronics: Samples are precut to a size of 4x4cm<sup>2</sup> using heavy plate shears
- b) Polymer Materials: Samples are precut to a size of 5x5mm<sup>2</sup> using heavy plate shears or/and scissors. Thin polymer foils are to be cut into small pieces with a shear.

### **5.5.3 Coarse grinding /milling**

Suitable for reduction of samples to ~ 1mm in diameter. Cool the samples if needed with the liquid nitrogen. For organic samples without metal content cryogenic milling is recommended. Then grind samples in mill using 4 mm stainless steel bottom sieve. Carefully sweep out and collect all particles. Refit mill with pre-weighed 1.0 mm stainless steel bottom sieve and reprocess the 4 mm material. Carefully sweep out mill and collect all particles. There is a 5 minutes cooling periods between grinding cycles.

### **5.5.4 Homogenizing**

Suitable for preparing the coarsely ground sample in the mixer prior to further size reduction in the centrifugal mill. Use a container with double capacity of the amount of powder to be mixed. Set mixer on middle speed setting by adjusting drive belts to the center of the drive pulleys. Mix powder for 45 minutes.

### **5.5.5 Fine grinding / milling**

Suitable for reduction of samples to < 1mm in diameter. Cool the homogenized sample powder with the liquid nitrogen if needed. For organic samples without metal content cryogenic milling is recommended. Be careful not to allow the liquid nitrogen to directly contact the powder to avoid spattering and sample loss. Mill the sample powder with centrifugal mill. Carefully sweep out centrifugal mill and collect all powder for assay.

### **5.5.6 Very Fine Grinding of Polymers and Organic Materials**

Suitable for reduction of samples as small as 500µm or less in diameter (not suitable for metal, glass, or similar hard-sharp materials). Approximately 3 - 10g of rough cut (3 – 5mm sections) of material to be ground is placed into the sample tube to about 2/3 to 3/4 full. Add grinding rod and secure ends of vial. Cool the Bladeless cryogenic impact grinder from room temperature for 15 minutes by filling the reservoir, placing grinding vials with samples in the

mill, locking cover into place. Pre-cool sample for 15 minutes and initiate a minimum of four two minute grinding cycles with 2 minute cooling cycles in between.

## 6 Screening by XRF Spectroscopy

### 6.1 Scope

This document describes the procedure for the screening analysis of regulated substances found in electro-technical products using the analysis technique of X-ray fluorescence (XRF) spectrometry. It covers all material types such as polymers, metals, and other electronic assembly materials.

The screening of a sample is performed using any XRF spectrometer, providing it has the performance characteristics described in this method. It must 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 electro-technical industry.

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

- Non-destructively - by directly measuring the sample as-is.
- Destructively - by going through a mechanical sample preparation step prior to analysis.

Usually, a screening of representative samples or uniform materials (such as plastics) can be done non-destructively, while for other samples (like a populated printed circuit board) mechanical sample preparation may be necessary. The XRF technique requires that the sample be of uniform composition.

Screening analysis allows one to distinguish between samples in three basic classifications:

- Pass- samples that safely contain concentrations, which are below the threshold values.
- Fail- samples that are clearly higher than the threshold values.
- Inconclusive- samples that require additional investigation, due to inconclusive analysis results.

It must be noted that X-ray fluorescence spectrometric analysis only provides information on the presence of regulated substances in their elemental form. Therefore, special attention is needed when analyzing for Chromium and Bromine, where the result will reflect the determination of presence or absence of total Chromium and total Bromine, and not that for the regulated hexavalent chromium and PBB/ PBDE. Thus, the absence or presence of hexavalent chromium, PBB, or PBDE must be confirmed with verification test procedure, if the presence of Chromium or Bromine is detected above the threshold value. On the other hand it must be noted that the presence of hexavalent chromium, PBB and PBDE is not possible if chromium and bromine are not detected in elemental form. (Note: In the case of a coating or thin film special care must be taken to ensure the XRF has sufficient sensitivity to detect especially thin or low concentration samples. See Annex)

Since XRF Spectrometry is a comparative technique, its performance depends on the quality of calibration, which in turn depends on the accuracy of the standards used to establish instrument calibration. XRF Analysis is very much matrix sensitive. This means that spectral as well as matrix interferences (such as absorption and enhancement phenomena) must be taken into account during analysis, especially of such diverse and complex samples as polymers and electronic components.

### 6.2 Normative references

The following referenced documents may be helpful 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.

- a) ASTM C 982 Guide for Selecting Components for Energy-Dispersive X-Ray Fluorescence Systems, Annual Book of ASTM Standards, Vol. 12.01
- b) C1118-89(2000) Standard Guide for Selecting Components for Wavelength-Dispersive X-Ray Fluorescence Systems
- c) Bertin, E.P. "Principles and Practices of X-Ray Spectrometric Analysis" ed 2 Plenum Press N.Y.
- d) Buhrke V.E., Jenkins, R., Smith D.K., "A Practical Guide for the Preparation of Specimens for X-ray Fluorescence and X-ray Diffraction Analysis" Wiley-VCHR.
- e) R. Van Grieken and A. Markowicz "Handbook of X-Ray Spectrometry" 2<sup>nd</sup> Addition, Marcel Dekker Inc.
- f) IUPAC Golden Book
- g) IUPAC data interpretation recommendations

### 6.3 Terms and definitions

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

- a) X-ray fluorescence spectrometry: A comparative analytical technique in which sample of material is irradiated under strictly controlled conditions by a beam of x-rays or low energy gamma rays in order to induce the emission of characteristic X-rays by the elements in the sample. The energy of these characteristic X-rays is specific to each element while their intensity can be correlated to the element concentration in sample. The process of emission of the characteristic X-rays is called X-Ray Fluorescence, or XRF. There are two practical realizations of the XRF Spectrometry wavelength-dispersive (WDXRF) and energy-dispersive (EDXRF).
- b) Source of X-ray excitation: X-ray tube or radioisotope is commonly used as source of X-ray excitation.
- c) X-ray detector: Device used to convert energy of an X-ray photon into corresponding electric pulse of amplitude proportional to photon energy. The X-ray fluorescence spectrometer must utilize a detector with the capability to resolve all spectral lines required, such that it may properly analyze the sample in accordance with the screening limits listed in table 3 (refer to annex for performance requirements).

### 6.4 Apparatus/Equipment and Materials

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

NOTE: XRF utilizes radiation, which is dangerous to humans. Therefore all radiation producing instruments should always be operated in accordance with safety instructions provided by manufacturer and in a strict adherence to the local health and occupational safety regulations as mandated by appropriate authorities. In addition, the personnel using the equipment should be properly trained in pertinent safety matters.

### 6.5 Test Procedure

#### 6.5.1 Preparation of the Spectrometer

- a) Power on the instrument according to the operation manual of instrument. Let the instrument warm up and stabilize as per the manufacturer's guidelines.
- b) To assure measurement stability, stability of the detector should be achieved, as specified by the manufacturer's guidelines.

#### 6.5.2 Calibration

- a) Follow the guidelines in the instrument's users manual when selecting the calibration samples using internal or commercially available reference samples. The element concentrations must vary independently in the calibration samples. If the calibration covers many elements in a wide range of concentrations, a big number of calibration samples may be necessary. The number of calibration samples can be significantly reduced by:

- calibration with fundamental parameters method (standardless)
- calibration with fundamental parameters method with a similar standard
- analysis using fundamental parameters plus empirical calibrations

NOTE: The analytical lines should be selected so as to keep spectral interference effects as low as possible. A list of recommended analysis lines is given in the annex to this chapter.

- b) The analytical method must be calibrated taking into account spectral interferences, matrix effects and other effects, which could influence the determination of the intensity of the fluorescence radiation from the spectra. A list of these effects can be found in the annex to this chapter.
- c) In order to assure sufficient analytical performance for each measured element, the measurement conditions of the instrument should be optimized by proper selection of excitation parameters. These conditions are instrument specific. Typically, this information is found in analyzer's instruction manual.
- d) As a general guidance, the user of this method is advised that inter-element spectral interference and matrix variations from sample to sample significantly affect the accuracy, precision, and minimum detection limit of each analyte. For example, it is feasible to achieve a 15 mg/kg Detection Limit for Cd in pure polyethylene, but not when 10% Br-compound and/or 2% of antimony are present. Further information can be found in the annex.

### 6.5.3 Verification of Spectrometer performance

Whether or not the apparatus to be used meets the required performance criteria must be determined by measuring standard reference material or comparable reference sample. It is recommended that the reference material be as close as possible to the matrix of the unknown sample of interest. The elements contained in such sample must be present at concentrations levels that are not greater than 3 to 5 times the screening limits for elements tested (see Table 3). The results obtained from reference sample must agree within the error of measurement with accepted concentration values for that sample. Only then, may the apparatus be used for analysis of the unknown material. Some manufacturers may provide, with the instrument, a Standard Operating Procedure (SOP) as well as an appropriate reference sample. Following the recommendation contained in such document assures the operator of the best possible quality of analytical results.

### 6.5.4 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 must be placed inside the specimen chamber of the X-ray fluorescence spectrometer. The total sample should be placed in such a way that the specimen of interest can be properly placed in measuring position. Measurement is conducted accordingly. If the specimen does not fit properly in the chamber, it must be cut to appropriate size for measurement. Alternatively, in order to avoid cutting of the sample, a portable XRF analyzer might be used for analysis. Specimens that are too small or very thin may violate the condition of minimum sample thickness or mass that must 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. (See Annex for further clarification and examples.)
- b) If the measurement is to be performed with a portable, hand held XRF analyzer, care must be taken to make sure that the analyzer's measuring window can be placed against the sample tested, in direct contact with it. Small and very thin samples must be presented for analysis as described in section a) above. Then, the analysis is performed with help of an additional accessory (if such is made available with the analyzer) that allows hand held analyzer to measure samples in sample cups. All provisions about minimum sample size/mass/thickness apply also to portable analyzers.
- c) If the specimen is in liquid, powder or pellet form or if it is a very small component, it is measured in the disposable sample cup fitted with disposable window film, which should

not be reused. When handling the window film, attention must be paid not to contaminate its surface by touching it.

### 6.5.5 Screening test

- a) Perform measurement for a specified period of time.
- b) Display and record analytical results.

### 6.5.6 Interpretation of results

Independent of which type of XRF spectrometer is used; the analytical method will allow the user to classify samples into one of three categories:

- a) "PASS" - If the result of the quantitative analysis, for all elements, is lower than the lower limits listed in table 2, the sample is tested "PASS".
- b) "FAIL" - If the result of the quantitative analysis, for any of the elements Hg, Pb or Cd, is higher than the higher limits listed in table 2, the sample is tested "FAIL".
- c) "INCONCLUSIVE" - If the result of the quantitative analysis, for any of the elements Hg, Pb or Cd, is in the region defined as intermediate, or if the result of the elements Br and Cr is higher than the higher limits listed in table 2, the analysis is inconclusive. Additional investigation must be performed. The test is "INCONCLUSIVE".

**Table 2: Screening limits in mg/kg for regulated elements in various matrices.**

Element	Polymer Materials	Metallic Materials	Electronics
Cd	$P \leq (70-3\sigma) < X < (130+3\sigma) \leq F$	$P \leq (70-3\sigma) < X < (130+3\sigma) \leq F$	$LOD < X < (250+3\sigma) \leq F$
Pb	$P \leq (700-3\sigma) < X < (1300+3\sigma) \leq F$	$P \leq (700-3\sigma) < X < (1300+3\sigma) \leq F$	$P \leq (500-3\sigma) < X < (1500+3\sigma) \leq F$
Hg	$P \leq (700-3\sigma) < X < (1300+3\sigma) \leq F$	$P \leq (700-3\sigma) < X < (1300+3\sigma) \leq F$	$P \leq (500-3\sigma) < X < (1500+3\sigma) \leq F$
Br	$P \leq (300-3\sigma) < X$		$P \leq (250-3\sigma) < X$
Cr	$P \leq (700-3\sigma) < X$	$P \leq (700-3\sigma) < X$	$P \leq (500-3\sigma) < X$

The screening limits are listed table 2. The common legal limits for the substances of interest have been assumed, but the "action levels" for this method have been set for the purpose of this screening procedure with a 30% (50% for electronics) margin of safety, such that a "PASS" (P) or "FAIL" (F) determination will be set at 30% (50% for electronics) less than or greater than the legal limit respectively. The margins have been agreed upon based on experience of many experts and practitioners in the industry. The symbol "X" marks the region, where further investigation is necessary). The term "3σ" expresses the repeatability of the analyzer, where σ is determined as the standard deviation by an at least 7 times repeated measurement of a typical sample with no content of the regulated substances (blank sample).

NOTE: The lower limit for Br in comparison to Hg, Pb and Cr is calculated based on the stoichiometry of Br in PBB/PBDE.

## 6.6 Method Evaluation

Precision and Bias of the method will be evaluated in a qualified round robin test.

## 6.7 Annex (informative)

### 6.7.1 Instrument Precision (3-sigma value in Table 2)

The term "3σ" expresses the repeatability of the analyzer, where σ is determined as the standard deviation of a series of 7 repeated measurements of a typical sample with no detectable (nearest zero) content of the regulated substances (blank sample). It is recommended that this sample be as close a possible to the matrix of the unknown samples being tested. All figures should be rounded to the nearest whole (non-decimal) mg/kg (part per million)

## 6.7.2 Recommended analysis lines in the XRF Spectrum

**Table 3: Characteristic X-ray lines for individual analytes.**

Analyte	Preferred Line	Secondary Line
Cadmium, Cd	K $\alpha$	
Lead, Pb	L $\beta$	L $\alpha$
Mercury, Hg	L $\alpha$	
Chromium, Cr	K $\alpha$	
Bromine, Br	K $\alpha$	K $\beta$

### 6.7.3 Matrix and Interference Effects

- 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
  - Metals: In metals samples the scattering of the primary radiation 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, ...
  - 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
  - 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 4: Effect of matrix composition on Limits of Detection of some controlled elements**

Element/Analyte	Pure Polymer	Polymer with $\geq 2\%$ Sb, no Br	Polymer with $\geq 2\%$ Br, no Sb
Cadmium	A	$\sim A \blacktriangleright 2A$	$\geq 2A$
Lead	B	$\sim 2B$	$\geq 3B$

NOTE: 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 5 above. The information in Table 5 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.

#### 6.7.4 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 CRT monitor cases, 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 must 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 must 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.

The numerical screening limits listed (table 3) 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.

In summary: 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.

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.

## 7 Determination of PBB and PBDE in Polymer Materials by GC/MS

### 7.1 Scope, Summary of Method and Application

This method is for determination of mono- to deca-bromiated biphenyl ether (BDE) and biphenyl (BB) of polymeric materials adopted in electro-technical appliances. The sample preparation should be begun with the identification of materials by infrared (IR) spectroscopy or equivalents methods. According to the information obtained, the solvents should be determined to dissolve the polymer. During the sample clean-up procedures, the matrix is removed by precipitation with non-solvents and conventional clean-up procedures including gel purification. For the certain polymers which can't be dissolved with usual solvents, the sample is grinded by cooling and milling followed by soxhlet extraction. After proper sample preparation and clean up procedures the sample extracts are analyzed by gas chromatography/mass spectrometry (GC/MS). An individual isomer is identified by comparing the GC retention time and ion abundance ratio of selected ions with the corresponding retention time and mass spectra of authentic standard compounds. Quantitative analysis is performed using selected ion current profile comparing with that of authentic standard compounds.

This method is best used for the most of polymers which are dissolved in solvents completely or partly dissolved like rubbers. The recovery of analyte can not be determined exactly with the polymers which are not dissolved in most of solvents.

### 7.2 References, Normative References, Reference Methods and Reference Materials

- a) EPA 1613: 1994: Tetra- through octa-chlorinated dioxins and furans by isotope dilution HRGC/HRMS.
- b) EPA 8270c:1996: Semivolatile organic compounds by gas chromatography and mass spectrometry.
- c) Certificate of analysis/documentations: Wellington laboratory, Southgate Dr. Guelph ON Canada.
- d) J. Brandrup, E.H. Immergut, E.A. Grulke. Polymer handbook. 1999. VII/497-VII/545.
- e) Reference and handling guide (GC/MS characterization and analysis of selected halogenated aromatic compounds): Wellington laboratory, Southgate Dr. Guelph ON Canada.
- f) Protocol from BAM (Determination of penta BDEs and Octa BDEs in polymers)
- g) Reference materials:
  - BDE-MXE (native BDE mixture) from Wellington laboratory
  - BDE-MXD (native BDE mixture ) from Wellington Laboratory
  - MBDE-MXE (<sup>13</sup>C<sub>12</sub> mass labeled BDE mixture) from Wellington laboratory
  - BDE-CVS-E (1-5: Calibration solution) from Wellington laboratory
  - MBDE-139-IS (<sup>13</sup>C<sub>12</sub> mass labeled hexa bromo diphenyl ether) from Wellington laboratory
  - RRT test Materials ABS, PS, PUR, Epoxy resin containing octa and penta BDEs from BAM

### 7.3 Terms and Definition

The definitions of the key terms used in this document are given below in alphabetical order.

- a) Analyte: PBDEs and PBBs tested for this method
- b) PFK (Perflurokerosene), PFTBA (Perfluorotributylamine): Compounds used to calibrate the exact m/z scale in the MS (PFK, PFTBA)

- c) Calibration solution: A solution prepared from a secondary standard and/or stock solutions and used to calibrate the response of the instrument with respect to analyte concentration
- d) Soluble polymer: Polymers which can be dissolved with the solvent(s) under the room temperature
- e) Partly soluble polymers: Polymers which are swelled in the solvents or part of the polymer is dissolved with solvents under the room temperature
- f) Non soluble polymer: Polymers which can not be dissolved with the solvents under the room temperature

## 7.4 Apparatus / Equipment and Materials

### 7.4.1 Apparatus

- a) Laboratory fume hood
- b) Balance ( precision 10mg)
- c) Glass disposable pipettes 150mm long x 5mm ID.
- d) Soxhlet apparatus with condenser ( 50~100ml of soxhlet extractor with 100ml or more round flask)
- e) Heating mantle to fit the round flask adopted at soxhlet apparatus
- f) Stirring apparatus for dissolving the polymers with magnet bar sealed in glass
- g) Rotary evaporator equipped with a variable temperature water bath and vacuum source
- h) Nitrogen blowing apparatus installed in a fume hood
- i) Oven capable of maintaining a constant temperature (105 –250°C)
- j) Furnace (400°C or higher)
- k) Glass ware: Glass funnel (125-1000ml), buchner funnel (15cm), Beaker (100-500ml), vials (1-2ml), washing bottles

### 7.4.2 Equipment

- a) Gas chromatography – temperature programmable with splitless injection port for capillary column
  - Column: (5%-phenyl)-methyl polysiloxane or 100% methyl polysiloxane and temperature limit of 340°C or more (length 15m; inner diameter 0,25mm; 0,1µm film thickness)
- b) Mass spectrometry – 70 e-volts (nominal) electron energy in the electron impact ionization mode with repetitively selectively ion monitoring 12 ions m/z minimum in a seconds. Scan range (200.0amu~800.0amu) Recommendation(200.0amu~960.0amu)

## 7.5 Reagents

- a) Calibration solution (Quantification solution)
  - Prepare in nonane or purchase as solutions or mixtures.
  - The commercially available calibration standard mixtures can be used such as BDE-MXE, BDE-MXD and BDE-CVS-E or equivalents.
- b) Sulfuric acid: Reagent grade or CMOS grade
- c) Purified nitrogen gas
- d) Solvents: GC grade or higher. A pesticide grade is recommended.
- e) Mainly used: Acetone, tetrahydrofuran, toluene, hexane, methylene chloride, chloroform, methanol. The solvent should be free of interferences.
- f) Quartz or glass wool: Rinsed with methylene chloride or baked at 400°C for 4 hours minimum
- g) Silica gel:

- Activated: 70~230 mesh, rinsed with methylene chloride, activated at 130°C for overnight and stored in a pre-cleaned glass bottle with screw cap that prevents moisture from entering
  - Acid silica gel: Mix 2.24g of activated silica gel with 1.76g of concentrated sulphuric acid
  - Basic silica gel: not recommended
- h) Water: Hexane cleaned water
- i) Recovery standard
- j) Labelled  $^{13}\text{C}_{12}$  BDEs or 4,4'-dibromooctafluoro biphenyl (f) or Penathrene D10 as recovery standard for the analysis of PBDEs. Labelled  $^{13}\text{C}_{12}$  PBB or 4,4'-dibromooctafluoro biphenyl (f) or Penathrene D10 as recovery standard for the analysis of PBBs

## 7.6 Sample Preparation

### 7.6.1 Sample Identification

Identify the sample with IR or equivalents methods. The solvents and non-solvents should be selected as according to the reference (d).

### 7.6.2 Extraction

The samples are grinded to a size of 1.0mm by the combination of cutting and mills under cooling with liquid nitrogen.

- a) For the soluble and partly soluble polymers
- Dissolve the milled samples (1.0g each) with 10ml of the selected solvents determined in section 7.6.1. Add the  $^{13}\text{C}_{12}$ -labeled PBDE(s) or the proper chemicals as recovery/internal standards. Stir it for 1 hour with glass sealed magnet bar.
  - Precipitate the polymers with non-solvents. Filter the suspensions through the quartz wool and Transfer the solution to separation funnel. Extract the compounds by liquid-liquid extraction or carry out the sample clean-up by gel-purification. Solid materials in quartz wool and the precipitated should be extracted by soxhlet. For these cases, 9 hrs of extraction or more extraction time is recommended.
  - After soxhlet extraction, the extract should be combined with filtrated solution and washed with  $\text{H}_2\text{SO}_4$  until colorless and then with hexane-rinsed water to make them neutral.
- b) For the non soluble polymers
- Without precipitation and liquid-liquid extraction, the milled samples should be extracted by soxhlet for 16 hours or more. For this case, toluene or tetrahydrofuran or 1:1 mixture of both solvents should be used as extraction solvents. After soxhlet extraction, the extracted should be combined with filtrated solution and washed with  $\text{H}_2\text{SO}_4$  until colorless and then with hexane-rinsed water to make them neutral. Add the  $^{13}\text{C}_{12}$ -labeled PBDE(s) or the proper chemicals as recovery/internal standards before starting the extraction.

### 7.6.3 Sample cleanup and purification

Stop the one end of a glass column (20mm X 350mm) with 250ml of reservoir with solvents rinsed glass wool. Add in sequence, 1g of dehydrated sodium sulfate, 1g of silica gel, 4g of acid modified silica gel, and 1g of dehydrated sodium sulfate. Rinse the column with 30ml of hexane and discard.

Add the sample concentrated at the previous steps. Elute the column with additional 130ml of hexane and retain the entire elute. Evaporate this solution to a volume of about 1~2ml and transfer to a glass bottle (6mm x 13mm) using glass disposable pipette.

## 7.7 Test Procedure

### 7.7.1 Calibration

- a) At least, five different calibration solutions each equidistant in concentration should be prepared within the range of linearity of the GC/MS.
- b) For the samples containing higher concentration of target isomers, the preparation of calibration solutions from the materials is recommended.

### 7.7.2 Instrument performance

Shall capable of scanning from 200 to 800 amu (recommendation: 960) and produce a mass spectrum for PFK or PFTBA (recommendation). High PFK and Super high PFK is recommended when exact determination of high molecular weight PBDEs or PBBs is needed.

WARNING: Usage of super high PFK can cause some damage to MS because of high viscosity.

### 7.7.3 Sample Analysis

- a) Inject 1.0µl of the concentrated samples containing the recovery standard solution using splitless injection. The volume injected must be the same with the volume used for calibration. The data collection can be stopped after deca BDE or deca BB were eluted. The column oven temperature is programmed as follows: 110°C (5min), 40°C/min up to 200°C (4.5min), 10°C/min to 325°C (15min). The injector temperature is held at 250°C. Mass spectrometry (GC/MS) analyses are performed on the following conditions.
  - Resolution ( 1,000m/e or more)
  - Ionization mode : Electron impact
  - Source temperature: 250°C (recommendation)
  - Monitoring mode: Selected ion monitoring. Exact masses of the ions monitored are presented in tables 5 and 6. For the  $^{13}\text{C}_{12}$  labeled internal standard, M+12 are selected.
- b) 1<sup>st</sup> analysis
  - Determine the concentration of the sample obtained from 7.6.2 and 7.6.3. Calculate the concentration/amount of the analytes using the following equations (1&3). If the concentration is over the threshold value (1,000ppm), the further process is not necessary. If not, 2<sup>nd</sup> analysis should be done.

NOTE: The operator should know the detection limit of the instruments

- c) 2<sup>nd</sup> analysis (for the confirmation and low threshold: 100~500ppm as total)
  - Concentrate the sample extract to about half of original solution volume. (For 100ppm: 1/10)
  - Weight the sample and determine the vol. using the density of solvents.
  - Analysis the sample using the same methods.

### 7.7.4 Calculation of Analytical Results

Prepare the calibration curve for each compound to be determined (Linear regression of the calibration measurements)

- a) Equation 1 : the measurement of quantification solutions
  - $Y = AX + B$
  - Y: area of each isomers
  - A= angular coefficient
  - X= concentration of each PBDE in the solutions
  - B= axis intercept
- b) Equation 2 :  $R = R_{sm}/R_{st}$  (Option)

- R = Recovery rate
- Rsm = area of recovery standard in standard solutions.
- Rst = area of recovery standard in sample.

c) Equation 3 : Determination of unknown content of sample (ppm)

- $C \text{ (ppm)} = [(Y_s - B)/A] * R * W_{cf}$
- C(ppm) = Unknown content of sample.
- Ys= area of the isomer of the sample
- Wcf = conversion factor (must including w/v  $\diamond$  w/w)

### 7.7.5 Quality Control

- a) Analysis of method blank have to demonstrate freedom from interfaces (US EPA 1613, Section 4.3 and 8270c)
- b) Three or five reference signals from PFTBA or PFK should be close to the theoretical value at the required resolving power.
- c) The blank and sample should be processed through the same steps to check for contamination and losses in the preparation processes.
- d) The blank sample should be injected before and after the sample analysis.

### 7.8 Evaluation of the Method

This method is evaluated by sixteen Korea analytical institutions and SAMSUNG electronics.

### 7.9 Annex

**Table 5: Reference masses for the quantification of PBDEs**

	IONS Monitored in the extract		
Mono-BDEs	<b>247.9</b>	249.9	
Di-BDEs	325.8	<b>327.8</b>	<u>329.8</u>
Tri-BDEs	403.8	<b>405.8</b>	<u>407.8</u>
Tetra-BDEs	323.8	<b>325.8</b>	<u>483.7</u>
Penta-PDEs	401.7	<b>403.7</b>	<u>561.6</u>
Hexa-BDEs	481.6	<b>483.6</b>	<u>643.5</u>
Hepta-BDEs	559.6	<b>561.6</b>	<u>721.4</u>
Octa-BDEs	639.5	<b>641.5</b>	<u>643.5 (801.3)</u>
Nona-BDEs	717.4	<b>719.4</b>	<u>721.4 (879.2)</u>
Deca-BDEs	797.3	<b>799.3</b>	<u>799.3 (231.8, 398.6, 400.5, 959.1)</u>

( ): Optional ions; Bold: Quantification ions; Under line: Identification ions.

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

	IONS Monitored in the extract		
Mono-BBs	<b>231.9</b>	233.9	
Di-BBs	309.8	<b>311.8</b>	<u>313.8</u>
Tri-BBs	387.8	<b>389.8</b>	<u>391.8</u>
Tetra-BBs	307.8	<b>309.8</b>	<u>467.7</u>
Penta-BBs	385.7	<b>387.7</b>	<u>545.6</u>
Hexa-BBs	465.6	<b>467.6</b>	<u>627.5</u>

Hepta-BBs	543.6	<b>545.6</b>	<u>705.4</u>
Octa-BBs	623.5	<b>625.5</b>	<u>627.5</u>
Nona-BBs	701.4	<b>703.4</b>	<u>705.4 (863.4)</u>
Deca-BBs	781.3	<b>783.3</b>	<u>785.3 (943.1215.8, 382.6,384.5)</u>

( ): Optional ions; Bold: Quantification ions; Under line: Identification ions.

## **8 Determination of PBB and PBDE in Polymer Materials by High Pressure Liquid Chromatography with Ultraviolet Detection (HPLC/UV)**

### **8.1 Scope, Application and Summary of Method**

This method provides procedures for the determination of PBB and PBDE in polymer materials. This document describes a material assay method for the identification of PBB/PBDE type of flame-retardants in polymers and Printed Wiring Boards. The test method applies High Pressure Liquid Chromatography with Ultraviolet Detection (HPLC/UV) for the analysis of Polybrominated Biphenyls PBB and Polybrominated Biphenyl Oxides PBDEs in polymers.

Analytes are Polybrominated Biphenyls PBB and Polybrominated Biphenyl Oxides PBDEs. The most frequently occurring PBBs are Octabromodiphenyl OBB and Decabromodiphenyl DBB. The most frequently occurring PBDEs are: Octabromodiphenyl oxide OBDE and Decabromodiphenyl oxide DBDE

### **8.2 References, Normative References, Reference Methods and Reference Materials**

- a) M. Riess and R. van Eldik, Identification of brominated flame-retardants in polymeric materials by reversed phase liquid chromatography with ultraviolet detection, Journal of Chromatography A 827 (1998) 65-71

### **8.3 Terms and Definitions**

- a) N/A

### **8.4 Apparatus / Equipment and Materials**

#### **8.4.1 Apparatus / Equipment**

- a) Extraction Unit: Precision heating block for extraction under reflux
- b) HPLC apparatus with pump (all pumps other than syringe pump) and with scanning or diode array detector
- c) Further typical laboratory tools and equipment is necessary
- d) The instrumentation can be replaced by items with similar functionality

#### **8.4.2 Materials**

- a) Volumetric flasks
- b) Adjustable Pipettes
- c) 12x32 mm vials
- d) Filter discs
- e) Stationary phase: modified C18 column

### **8.5 Reagents**

- a) Methanol (HPLC grade)
- b) Water (HPLC grade)
- c) KH<sub>2</sub>PO<sub>4</sub> p.A.
- d) NaHPO<sub>4</sub> p.A.
- e) DE-USC 902 Decabromodiphenyl ether (technical) (DE-83R-Great Lakes) (e.g LGC-Promochem)
- f) U-RBF-074 Octabromobiphenyl (technical) (FR250 BA, Dow Chemicals) (e.g LGC-Promochem)
- g) DE-USC 910 Octabromodiphenylether (technical) (DE-79-Great Lakes) (e.g LGC-Promochem) (U-RBF-102 Decabromobiphenyl) (e.g LGC-Promochem)



### 8.5.1 Standard preparation / Stock solution preparation

- h) Mobile Phase: 97% Methanol and 3% of buffered water. A phosphate buffer is used. The water was buffered by dissolving 0.1509 g KH<sub>2</sub>PO<sub>4</sub> and 0.2477 g NaHPO<sub>4</sub> in 100ml of water. The run time is 12 min at a flow rate of 1ml/min.
- i) As sample solvent for the dissolution of pure standards and for the extraction of samples n-Propanol was used.

### 8.6 Sample Preparation

Samples to be investigated are ground in a centrifugal mill to the grain size of 1 mm, partly under cooling with liquid nitrogen. 100mg of the sample is extracted in a soxhlet extractor for three hours using 70ml of n-Propanol. After cooling to room temperature the extracts are filtered and filled up to a volume of 100ml. Additional concentration steps and higher sample mass might be necessary if the flame retardant concentration is close to the threshold limit in the sample.

As sample solvent for the dissolution of pure standards and for the extraction of samples n-Propanol was used.

### 8.7 Test Procedure

#### 8.7.1 Calibration

The use of a diode array detector is recommended for the correct identification of unknowns. Commercial technical standards are used for calibration of retention time, UV spectra and peak area/concentration.

#### 8.7.2 Instrument performance

For the HPLC measurement and data evaluation the instrument supplier instructions are followed. Internal Reference Samples and Commercial Standards might be used as References.

#### 8.7.3 Sample Analysis

The method is suitable for the flame-retardant classes Polybrominated Biphenyls PBB, Polybrominated Biphenyl Oxides PBDE. The standard used for PBB (Polybrominated Biphenyls) is Octabromobiphenyl (OBB). The standards used for PBDE (Polybrominated Diphenyl Ethers) are Decabromobiphenyl Oxide (DECA) and Octabromodiphenyloxide (OCTA).

OBB is the only Polybrominated Biphenyl frequently used in technical plastics. OBB as technical product not only consists of the Octa brominated compound but also contains the Hepta- and Hexa- derivate, due to the technical grade and way of production.

This is similar for OCTA that belongs to the class of Polybrominated Diphenyl Oxides. It contains the Nona- Octa- Hepta- and Hexa- brominated compounds. Decabrominated Diphenyl Oxide (DECA) also belongs to the Polybrominated Diphenyl Oxides and consists of the Deca- as well as of the Nona brominated compound.

For the HPLC measurement and data evaluation the instrument supplier instructions are followed. The use of a diode array detector is recommended for the correct identification of unknowns. Commercial technical standards are used for calibration of retention time, UV spectra and peak area/concentration.

Draw into a new, unused syringe approximately 3ml of sample and attach a syringe filter to the syringe. Discard 0.5ml through the filter and load the remaining sample (equal to at least 10X the sample loop volume) into sample loop. Samples having concentrations higher than the established calibration range must be diluted into the calibration range and re-analyzed.

Each sample should be injected twice and the Relative Standard Deviation of the duplicates should be less than 20% or the sample data must be qualified.

#### 8.7.4 Calculation of Analytical Results

Appropriate use of the software and references to the calibration standards might be used to calculate the results.

#### 8.7.5 Test Report

The report shall give the average concentration together with the uncertainty of the measurement. HPLC is preferably used to identify the species. Additional quantitative data can be obtained from ED-XRF measurements.

#### 8.7.6 Quality Control

The laboratory that implements this method should work according to internationally accepted quality standards and therefore use appropriate validation procedures and should document the method setup in detail. It is recommended to work according to GLP standards.

- a) The documentation of quality for this method shall include:
- b) Retention time repeatability
- c) Peak Area repeatability
- d) Calibration function
- e) Linear Range
- f) Limit of detection in sample material

Frequent recalibration including measurements of internal control samples and Null values shall be included to make sure the instrument is running properly.

### 8.8 Evaluation of the Method

The method was established using commercial technical pure flame-retardants as references and real material standards for comparison.

The basic retention time data obtained for the pure reference substances were measured under the conditions described above are listed in table 7. This table also sums up the retention time stability data. Five injections were performed per substance. The measurements do include variations from day to day. Complete UV-spectra are recorded for the standards and stored in a UV-Spectral database.

**Table 7: Retention time Data**

	Retention time AV (n=10)	SD (n=5)	RSD	Theoretical Number of Plates	Peak width [min]
TBBPA	0,891	0,012	1,37%	291	0.21
OBB	5,884	0,102	1,73%	1049	0.72
DECA	9,043	1,53	1,69%	2608	0.72
OCTA	5,651	0,087	1,54%	837	0.84

Table 8 shows some exemplary results for the peak area reproducibility. Other wavelengths can be extracted from the three-dimensional chromatogram at any time. The three dimensional chromatograms are recorded using 2nm resolution. Each of the wavelengths can be extracted from the data field.

**Table 8: Peak Area Reproducibility Data**

	Peak Area AV (n=5)	SD (n=5)	RSD
TBBPA (10mg/100ml), λ quant. = 254 nm	29,683	0,156	0,52%
OBB (12mg/100ml), λ quant. = 210 nm	70,346	0,574	0,82%
DECA (1mg/100ml), λ quant. = 210 nm	4,321	0,156	3,62%
OCTA (2,5mg/100ml), λ quant. = 210 nm	15,498	0,043	0,28%

The quantification of the flame retardants is limited using HPLC because the relative amount of lower or higher brominated constituents in these technical products is varying depending on the producer or process used for production of these flame retardants. As soon as the producer is different from the one that manufactured the standard used for calibration, the peak areas of the chromatogram “fingerprint” may vary. Therefore the molecular mass of the compounds is not known what makes it necessary to use concentration units of mass per volume [mg/100ml] instead of concentration units in mol/l. The identification of these compounds may be easier at the same time due to the chromatogram fingerprint comparison of retention time data that can be done due to this effect.

The quantification of DECA using HPLC is limited in the linear range, due to the limited solubility. The quantification is much easier using the bromine concentration from XRF measurements.

## **9 Test for the Presence of Hexavalent Chromium (Cr VI) in Colorless and Colored Chromate Coating on Metallic Samples**

### **9.1 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. Due to its highly reactive nature, the concentration of hexavalent chromium in a chromate coating layers can change drastically with time and storage conditions. Therefore, the samples shall be stored at ambient conditions and the analytical method described here shall be carried out within 30 days of the coating process. Ambient conditions are defined as: humidity 45-75%, temperature 15-35°C.

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, the boiling-water-extraction procedure shall be conducted for verification. When the presence of hexavalent chromium in a sample is detected using this method, the sample is considered to have a hexavalent chromium coating.

Hexavalent chromium is toxic to human beings and classified as mutagenic and carcinogenic. All potential Cr (VI) containing samples and reagents used in the method shall be handled with appropriate precautions.

This method is adopted from ISO 3613: 2000(E), "Chromate Conversion Coatings on Zinc, Cadmium, Aluminum-Zinc Alloys and Zinc-Aluminum alloys---Test Methods".

### **9.2 References, Normative References, Reference Methods and Reference Materials**

- a) ISO 3613: 2000(E), "Chromate Conversion Coatings on Zinc, Cadmium, Aluminum-Zinc Alloys and Zinc-Aluminum Alloys---Test Methods"
- b) ZVO-0102-QUA-02 "Qualitative Analysis of Cr-VI in Passivation Layers on Parts by Spot Analysis"
- c) GMW3034 "Absence of Hexavalent Chrome (VI) Coatings"
- d) DIN 50993-1 "Determination of Hexavalent Chromium in Corrosion Protection coatings-Part 1: Qualitative Analysis"

### **9.3 Terms and Definitions**

The definitions of the key terms used in this document are given below

- a) N/A

### **9.4 Apparatus / Equipment and Materials**

- a) Calibrated balance: an analytical balance with an accuracy of 0.1mg.
- b) Thermometer or thermistor or other temperature measurement device: capable of measuring up to 100°C.
- c) Colorimetric equipment: either a spectrophotometer, for use at 540nm, providing a light path of 1cm or longer; or a filter photometer, providing a light path of 1cm or longer and equipped with a greenish-yellow filter having maximum transmittance near 540nm.
- 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: H<sub>2</sub>O, 1:2:9) followed by rinsing with tap water and reagent 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, 100ml, or equivalent of acceptable precision and accuracy.
- f) Assorted calibrated pipettes: Class A glassware or equivalent of acceptable precision and accuracy.
- g) Digestion vessel: borosilicate glass or quartz with a volume of 250ml or equivalent.

## 9.5 Reagents

- a) 1,5-diphenylcarbazide, analytical reagent grade.
- b) 1mg/kg  $K_2Cr_2O_7$  standard solution: dissolve 0.113g  $K_2Cr_2O_7$ , analytical reagent grade, in DI water and dilute it with DI water in a glass container to total weight of 100g. The shelf life of this solution is about 1 year. Measure 0.25g of this solution in a second glass container and dilute it with DI water to total weight of 100g.
- c) Acetone analytical reagent grade.
- d) Ethanol (96%), analytical reagent grade.
- e) Orthophosphoric acid solution (75%), analytical reagent grade.
- f) DI water, DI water shall be free of interferences.

## 9.6 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°C). The samples shall not be subject to forced drying at temperature in excess of 35°C. Treatment in alkaline solutions shall not be performed as 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.

## 9.7 Test Procedures

### 9.7.1 Spot-test Procedure

- a) Dissolve 0.4g of 1,5-diphenylcarbazide in a mixture of 20ml acetone and 20ml ethanol (96%). After dissolution, add 20ml of 75% orthophosphoric acid solution and 20ml of DI water. Prepare this solution not more than 8 hours prior to use.
- b) 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.
- 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 sample surface, 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 an analyst to judge, place 1 drop of  $K_2Cr_2O_7$  standard solution (1mg/kg concentration, prepared in 9.5 b) on a newly polished bare substrate, and mix it with 1 drop of test solution (prepared in procedure 9.7.1 a). Compare the color obtained from the sample with the color obtained from the  $K_2Cr_2O_7$  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 not, the test result is negative. The detection limit for the spot-test is 1mg/kg.
- 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.

### 9.7.2 Boiling-water-extraction procedure

- a) The sample to be tested shall have a surface area of  $(50 \pm 5)$  cm<sup>2</sup>. 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  $(50 \pm 5)$  cm<sup>2</sup>.
- b) Heat in a suitable beaker (with volume graduation) 50ml of DI water to boiling and totally immerse the sample(s) inside the beaker. Leach for exactly 5 minutes while the water continues to boil. Remove the sample(s), and cool the beaker and its content to room temperature. Fill up with DI water to 50ml if some water evaporated. If the solution is milky or has a precipitate, filter it through a paper filter (0.45µm pore size) into a dry beaker. Add 1ml of orthophosphoric acid solution (9.5 e) and mix well. Pour half the solution into another dry beaker. Add 1ml test solution (9.7.1. 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).
- c) If the color developed during the test is difficult for the analyst to judge, transfer a portion of the solution to an absorption cell. After a reaction time of 2 minutes, measure the absorbance in a colorimetric equipment against the blank.
- d) Dilute 1ml of 1mg/kg  $K_2Cr_2O_7$  standard solution (9.5 b) to 50ml with DI water. Add 1ml of orthophosphoric acid solution (9.5 e) and mix well. Add 2ml test solution (9.7.1 a), mix and measure the absorbance as above.
- e) If the absorbance value obtained in 9.7.2 c) is equal to, or greater than that obtained in 9.7.2 d), the sample is considered to have a hexavalent chromium coating. If not, the test result is negative. The detection limit for the boiling-water-extraction test is 0.02mg/kg with 50cm<sup>2</sup> sample surface area used.

### 9.8 Evaluation of the Method

The principle of this method was evaluated and supported by a study organized by IEC TC111 WG3. The study was focused on detecting the presence of Cr (VI) in metallic samples. There were fourteen international laboratories that participated in the study.

## 10 Determination of Hexavalent Chromium (Cr VI) by Colorimetric Method

### 10.1 Scope, Application and Summary of Method

This method describes the procedures to measure hexavalent chromium, i.e. Cr(VI), quantitatively in samples of polymer materials, and electronic components. Hexavalent chromium is toxic to human beings and classified as mutagenic and carcinogenic. 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 alkaline extraction solution is a mixture of 0.28 M Na<sub>2</sub>CO<sub>3</sub>/0.5 M NaOH. A sample of interest is digested in the solution at 90-95°C for 60 minutes.

The Cr(VI) concentration in the extract is determined by its reaction in acid 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 540nm.

If high levels of contaminations 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 derivatization of the Cr(VI) with diphenylcarbazide is followed by detection of the colored complex at 540nm.

Other alternative digestion methods or analytical techniques may be utilized once the performance effectiveness has been validated according to the performance based measurement system criteria (reference to section 10.6.5 Quality Control).

Possible interference 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 not limited to pH, ferrous iron, sulfide, hexavalent molybdenum, mercury salts, etc.

This method is adopted from US EPA 3060A and US EPA 7196A.

### 10.2 References, Normative References, Reference Methods and Reference Materials

- a) EPA method 3060A, "Alkaline Digestion for Hexavalent Chromium", December 1996.
- b) EPA method 7196A, "Chromium, Hexavalent (colorimetric)", July 1992.
- c) EPA method 7199A, "Determination of Hexavalent Chromium in Drinking Water, Groundwater and Industrial Wastewater Effluents by Ion Chromatography", December 1996.
- d) ISO 3613: 2000(E), "Chromate Conversion Coatings on Zinc, Cadmium, Aluminum-zinc Alloys and Zinc-aluminum Alloys---Test methods".
- e) Draft of VDA/ZVO instructions, "Qualitative and Quantitative Analysis of Hexavalent Chrome in Corrosion Protection Layers Part of 1: Qualitative Analysis". 1.1.1 Dated 13.03.2003, translated 16.09.2003.

- f) EPA method 218.6, revision 3.4. "Determination of Dissolved Hexavalent Chromium in Drinking Water, Groundwater, and Industrial Wastewater Effluents by Ion Chromatography", October, 1999.
- g) New Jersey Department of Environmental Protection and Energy (NJDEPE). NJDEPE modified methods 3060/7196. 1992.
- h) Vitale, R., Mussoline, G., Petura, J., James, B., 1993. A Method Evaluation Study of an Alkaline Digestion (modified method 3060) Followed by Colorimetric Determination (method 7196) for the Analysis for Hexavalent Chromium in Solid Matrices. Environmental Standards, Inc. Valley Forge, PA 19482.
- i) ASTM (American Society for Testing and Materials), 1981. Standard Practice for Oxidation Reduction Potential of Water. ASTM Designation: D1498-93.
- j) Vitale, R.J., Mussoline, G.R., Petura, J.C. and James, B.R. 1994. Hexavalent Chromium Extraction from Soils: Evaluation of an Alkaline Digestion Method. J. Environ. Qual. 23:1249-1256.
- k) U.S. Department of Health and Human Services - Agency for Toxic Substances and Disease Registry. Toxicological Profile for Chromium. April, 1993.
- l) James, B.R., Petura, J.C., Vitale, R.J., and Mussoline, G.R. 1995. Hexavalent Chromium Extraction from Soils: A Comparison of Five Methods. Environ. Sci. Technol. 29:2377-2381. CD-ROM 3060A-10 Revision 1. December 1996
- m) U.S. Environmental Protection Agency. 1993. IRIS: A Continuously Updated Electronic Database Maintained by the U.S. Environmental Protection Agency. National Library of Medicine, Bethesda, MD.
- n) Certified Reference Material BCR-680 and BCR-681 (Cr in polyethylene)
- o) Certified Reference Material BAM-S004 (glass containing hexavalent chromium)

### 10.3 Terms and Definitions

The definitions of the key terms used in this document are given below

- a) Calibration standard: A solution prepared from the dilution of stock standard solutions. The calibration standard solutions are used to calibrate the instrument response with respect to analyte concentration.
- b) Stock standard solution: A concentrated solution containing analyte(s) of interest prepared in the laboratory using creditable reference materials.
- c) Method detection limit: The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.
- d) Quality control sample: A solution of the method analyte of known concentration which is used to fortify an aliquot of laboratory reagent blank or sample matrix. The quality control sample is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check either laboratory or instrument performance.
- e) Laboratory duplicates: Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analysis of these two samples indicates precision associated with laboratory analytical procedures.
- f) Matrix: The material or substance, form or state in which the analyte is embedded.
- g) Matrix spike recovery: Recovery of a known amount of analyte added to sample. Determination of matrix spike recovery is based on results provided by spiked and unspiked sample. It is used to determine whether the sample matrix contributes bias to the analytical results.
- h) Laboratory reagent blank: The measured value obtained when a target analyte or parameter is not supposed to be present during measurement. It is used to monitor contamination and purity of test supplies and materials.
- i) Certified reference samples: Reference samples with concentration values certified by a recognized standards supplier, e.g. NIST, BAM etc.



## 10.4 Apparatus / Equipment and Materials

### 10.4.1 Apparatus / Equipment

- a) Vacuum filtration apparatus
- b) Heating and stirring device: Capable of maintaining the digestion solution at 90-95°C with continuous auto stirring capability or equivalent. A Teflon coated magnetic stirring bar can be used for polymer samples. However, it is not recommended for ferromagnetic samples, such as those commonly found in the metallic and electronic samples. In that case, an overhead stirrer with Teflon shaft and paddle is recommended.
- c) Calibrated pH meter: To read pH range 0-14 with accuracy  $\pm 0.03$  pH units.
- d) Calibrated balance: An analytical balance with an accuracy of 0.1 mg.
- 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.

### 10.4.2 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: H<sub>2</sub>O, 1:2:9) followed by rinsing with tap water and reagent 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.
- c) Assorted calibrated pipettes: of acceptable precision and accuracy.
- d) Digestion Vessel: Borosilicate glass or quartz with a volume of 250 ml or equivalent.
- e) Filter membranes (0.45  $\mu\text{m}$ ). Preferably cellulosic or polycarbonate membranes.

### 10.4.3 Reagents

- a) Nitric acid: concentrated HNO<sub>3</sub>, analytical reagent grade or spectrograde quality. Store at 20-25°C in the dark. Do not use concentrated HNO<sub>3</sub> if it has a yellow tinge; this is indicative of photoreduction of NO<sub>3</sub><sup>-</sup> to NO<sub>2</sub>, a reducing agent for Cr(VI).
- b) Sodium carbonate: Na<sub>2</sub>CO<sub>3</sub>, anhydrous, analytical reagent grade. Store at 20-25°C in a tightly sealed container.
- c) Sodium hydroxide: NaOH, analytical reagent grade. Store at 20-25°C in a tightly sealed container.
- d) Magnesium chloride: MgCl<sub>2</sub> (anhydrous), analytical reagent grade. A mass of 400 mg MgCl<sub>2</sub> is approximately equivalent to 100 mg Mg<sup>2+</sup>. Store at 20-25°C in a tightly sealed container.
- e) Phosphate Buffer:
  - K<sub>2</sub>HPO<sub>4</sub>: analytical reagent grade.
  - KH<sub>2</sub>PO<sub>4</sub>: analytical reagent grade.
  - 0.5 M K<sub>2</sub>HPO<sub>4</sub> / 0.5 M KH<sub>2</sub>PO<sub>4</sub> buffer at pH 7: Dissolve 87.09 g K<sub>2</sub>HPO<sub>4</sub> and 68.04g KH<sub>2</sub>PO<sub>4</sub> into 700ml of reagent water. Transfer to a 1l volumetric flask and dilute to volume.
- f) Lead Chromate: PbCrO<sub>4</sub>, analytical reagent grade. Store at 20-25°C in a tightly sealed container.

- g) Digestion solution: Dissolve  $20.0 \pm 0.05$  g NaOH and  $30.0 \pm 0.05$  g  $\text{Na}_2\text{CO}_3$  in reagent water in a 1l 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 must be checked before using. The pH must be 11.5 or greater, if not, discard.
- h) Potassium dichromate stock solution: Dissolve 141.4mg of dried potassium dichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$  (analytical reagent grade), in reagent water and dilute to 1l (1 ml =50µg Cr).
- i) Potassium dichromate standard solution: Dilute 10ml potassium dichromate stock solution to 100ml (1ml =5µg Cr).
- j) Sulfuric acid, 10% (v/v): Dilute 10ml of distilled reagent grade or spectrograde quality sulfuric acid,  $\text{H}_2\text{SO}_4$ , to 100ml with reagent water.
- k) Diphenylcarbazide solution: Dissolve 250mg 1,5-diphenylcarbazide in 50ml acetone. Store in a brown bottle. Discard when the solution becomes discolored.
- l) Potassium dichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$ , spiking solution (1000mg/l Cr (VI)): Dissolve 2.829g of dried (105°C)  $\text{K}_2\text{Cr}_2\text{O}_7$  in reagent water in a 1l volumetric flask and dilute to the mark. Alternatively, a 1000mg/l Cr (VI) certified primary standard solution can be used. Store at 20-25°C in a tightly sealed container for use up to six months.
- m) Potassium dichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$ , matrix spiking solution (100mg/l Cr (VI)): Add 10.0ml of the 1000mg Cr (VI)/l made from  $\text{K}_2\text{Cr}_2\text{O}_7$  spiking solution (section 10.5 l) to a 100ml volumetric flask and dilute to volume with reagent water. Mix well.
- n) Acetone: analytical reagent grade: Avoid or redistill material that comes in containers with metal or metal-lined caps.
- o) Reagent water - reagent water should be free of interferences.

## 10.5 Sample Preparation

Samples should be collected using devices and placed in containers that do not contain stainless steel.

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%, temperature 15-35°C.

Since the stability of Cr (VI) in extracts is not completely understood, the analysis should be carried out as soon as possible.

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).

Prior to digestion, polymer samples and electronic components shall be ground into a fine powder capable of passing through a size 500 m sieve, e.g. a brass or stainless steel #35 U.S. Standard Sieve.

## 10.6 Test Procedure

### 10.6.1 Extraction

- a) Take about 5g of sample and measure its weight accurately to 0.1mg. 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 5g (or another chose 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 (section 10.4.3 f) or 10.4.3 l).
- c) To each sample, add  $50 \pm 1$ ml of digestion solution (section 10.4.3.g)) measured with a graduated cylinder. Also add approximately 400mg of  $\text{MgCl}_2$  (section 10.4.3 d) and 0.5ml of 1.0M phosphate buffer (section 10.4.3 e) to each sample. It is optional to add  $\text{MgCl}_2$  in

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.

- d) Stir while heating the samples continuously to 90-95°C, then maintain the samples at 90-95°C for at least 60 minutes with constant stirring.
- e) Gradually cool, with continued agitation, each solution to room temperature. Transfer the contents quantitatively to the filtration apparatus; rinsing the digestion vessel with 3 successive portions of reagent water. Transfer the rinsates to the filtration apparatus. Filter through a 0.45µm membrane filter. If the filter becomes clogged using the 0.45µm 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 reagent water and transfer the filtrate and the rinses to a clean 250ml vessel. Keep the filtered solid on filter membranes for possible use in assessing low Cr(VI) matrix spike recoveries. Store the filtered solid at  $4 \pm 2^\circ\text{C}$ .
- f) With constant stirring, slowly add concentrated nitric acid solution to the 250ml vessel dropwise. Adjust the pH of the solution to  $7.5 \pm 0.5$ . Remove the stirring device and rinse, collecting the rinsate in the beaker. Transfer quantitatively the contents of the vessel to a 100ml volumetric flask and adjust the sample volume to 100ml with reagent water. Mix well. The sample digestates are now ready to be analyzed.

#### 10.6.2 Color development and measurement

- a) Transfer 95ml of the extract to be tested to a clean 100ml vessel. Add 2.0ml diphenylcarbazide solution and mix. Slowly add  $\text{H}_2\text{SO}_4$  solution to the vessel and adjust the pH of the solution to  $2 \pm 0.5$ . Transfer quantitatively the contents of the vessel to a 100ml volumetric flask and adjust the sample volume to 100ml with reagent water. Let stand 5 to 10 minutes for full color development.
- b) Transfer an appropriate portion of the solution to a 1cm absorption cell and measure its absorbance at 540nm 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.

#### 10.6.3 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 (section 10.4.3.i) in measured volumes into a 10ml volumetric flask to generate standard concentrations ranging from 0.1 to 5mg/l Cr (VI) when diluted to the appropriate volume. 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.
- c) Develop the color of the standards as for the samples.
- d) Transfer an appropriate portion of the solution to a 1cm absorption cell and measure its absorbance at 540nm in a colorimetric equipment.
- 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).

#### 10.6.4 Calculation of Analytical Results

- a) Cr (VI) concentration (ppm) in total sample
  - Cr (VI) concentration =  $(A \cdot D \cdot F) / S$ ; 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

- $RPD = \{ | (S-D) | / [(S+D)/2] \} * 100$ ; where:
- S = Initial sample result ( $\mu\text{g}$ )
- D = Duplicate sample result ( $\mu\text{g}$ )

c) Spike Recovery

- Spike Percent Recovery =  $\{(SSR-SR)/SA\} * 100$ ; where:
- SSR = Spike sample result ( $\mu\text{g}$ )
- SR = Unspiked sample result ( $\mu\text{g}$ )
- SA = Spike added ( $\mu\text{g}$ )

### 10.6.5 Quality Control

A minimum of one blank per sample batch must be prepared and analyzed to determine if contamination or any memory effects are occurring.

Laboratory Control Sample: as an additional determination of method performance, utilize the matrix spike solution (section 10.4.3 m) or solid matrix spiking agent  $\text{PbCrO}_4$  (section 10.4.3 f) to spike into 50ml of digestion solution (section 10.4.3 g) at a frequency of one per batch. Each patch shall contain  $\leq 20$  samples. 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 must be analyzed at a frequency of one per batch. Duplicate samples must have a Relative Percent Difference of  $\leq 20\%$ .

A soluble or insoluble pre-digestion matrix spike sample must be analyzed at a frequency of one per batch. Each patch shall contain  $\leq 20$  samples. The soluble matrix spike sample is spiked with 1.0ml of the matrix spiking solution (section 10.4.3 m) or at twice the sample concentration, whichever is greater. The insoluble matrix spike is prepared by adding 1-2mg of  $\text{PbCrO}_4$  (section 10.4.3 f) 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  $\geq 0.99$ , or a new calibration curve should be built.

Verify calibration with an independently prepared check standard for every 20 samples. The relative percent difference of original standard and check standard should be  $\leq 10\%$ , or a new calibration curve should be built.

Dilute samples if they are more concentrated than the highest calibration standard.

An alternative digestion or measurement method shall be allowed if it meets all the quality control criteria listed above, i.e. Performance Based Measurement System is acceptable to the Cr (VI) analysis.

### **10.7 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.

## **11 Determination of Mercury in Polymer Materials, Metallic Materials and Electronics by CV-AAS, AFS, and ICP-AES/MS**

### **11.1 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 polymer materials, metal materials and electronics (printed wiring boards, cold cathode fluorescent lamps, mercury switches). Batteries containing mercury are to be handled as described in the “Standard Analytical Method” of the Battery Industry (Reference b).

The standard describes the use of four methods (CVAAS, Cold Vapor Atomic Absorption Spectrometry, AFS, Atomic Absorption Spectrometry, ICP-AES(-OES), Inductively Coupled Plasma-Atomic Emission Spectrometry), and ICP-MS) and several procedures for preparing the sample solution, from which the most appropriate way of analysis can be selected by experts.

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 CVAAS, AFS, ICP-AES(-OES) or ICP/MS. For AFS and ICP-AES(-OES)/MS, the digestion solution may be analyzed straightway. By using CVAAS (cold vapor atomic absorption spectrometry) technique, 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 by the use of different analytical means that no target elements are included in these 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 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.

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 must 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 must 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.

### **11.2 References, Normative References, Reference Methods and Reference Materials**

- a) 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.

- b) Battery Industry (EPBA, BAJ and NEMA), 1998, Standard Analytical Method for the Determination of Mercury, Cadmium and Lead in Alkaline Manganese Cells using AAS, ICP-AES and “Cold Vapor”.
- c) US EPA SW-846 Method 3050B, Acid digestion of sediments, sludges and soils
- d) US EPA SW-846 Method 3052, Microwave assisted acid digestion of siliceous and organically based matrices
- e) US EPA SW-846 Method 7000, Series measurement methods for lead, cadmium, chromium, & mercury
- f) US EPA SW-846 Method 6010B, Inductively coupled plasma-atomic emission spectrometry
- g) US EPA SW-846 Method 7471A, Mercury in solid or semisolid waste (manual cold-vapor technique)
- h) US EPA SW-846 Method 7470A, Mercury in liquid waste (manual cold-vapor technique)
- i) US EPA SW-846 Method 7474, Mercury in sediment and tissue samples by atomic fluorescence spectrometry
- j) BCR-680, BCR-681: Certified Reference Material for Plastics packaging and packaging material; certification of mass fractions of As, Br, Cd, Cl, Cr, Hg, Pb and S in polyethylene.

### 11.3 Terms and Definitions

The definitions of the key terms used in this document are given below

- a) CCFL(s): Cold cathode fluorescent lamp(s)
- b) PWB(s): Printed wiring board(s)
- c) ICP-AES (-OES), Inductively coupled plasma atomic emission spectroscopy: Method of determining the target element contained in the sample by means of atomization and ionization of the sample with high-frequency plasma. The energy emitted by excited atoms or ions is measured. The wavelengths of the emitted energy are specific to the elements present in the sample.
- d) CVAAS, Cold vapor atomic absorption spectrometry: This technique is based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak area) is measured as a function of mercury concentration.
- e) AFS, atomic fluorescence spectrometry: This technique is based on the optical emission from gas-phase atoms that have been excited to higher energy levels by absorption of electromagnetic radiation. Analysis of solutions or solids requires that the analyte atoms be desolvated, vaporized, and atomized at a relatively low temperature in a heat pipe, flame, or graphite furnace. A hollow-cathode lamp or laser provides the resonant excitation to promote the atoms to higher energy levels. The atomic fluorescence is dispersed and detected by monochromators and photomultiplier tubes, similar to atomic-emission spectroscopy instrumentation.
- f) ICP-MS, Inductively coupled plasma mass spectrometry: Method of determining the target element contained in the sample by means of ionizing the sample with high-frequency plasma. The generated ion is measured with mass spectrometer for the number of ions in mass-to-charge ratio ( $m/z$ ) of the target element for analysis of the element or its isotope.
- g) Memory effect: Phenomenon caused by presence of elements in sample or standard calibration solution analyzed previously in the high-frequency plasmaspectrometer or accompanying device, causing partial overlap with target element spectral signal in the current analyte.
- h) Calibration standard: Solution containing existing concentration of method analytes for developing a calibration curve.
- i) Calibration blank: Solution identical in composition as a calibration standard with zero concentration of method analytes.

- j) Internal standard element: Elements added in identical concentrations in calibration standard, calibration blank and sample solution, in order to adjust non-spectral interference and time-series change in the sensitivities of the used analytical equipment.
- k) Detection limit: Concentration able to produce triple the standard deviation for the intensities of either the atomic spectra lines (ICP/AES (-OES) and AAS) or the intensities of the selected mass-to-charge ratios (ICP/MS) or background intensity when calibration blank is measured 10 times in succession.
- l) Quality control: Procedure to guarantee that analysis has been conducted precisely in compliance with specified standards, in order to assure data reliability.

#### 11.4 Apparatus / Equipment and Materials

- a) Scale: Precision level of 0.1mg
- 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 vessels (for the digestion of polymers)
- d) Inductively Coupled Plasma-Atomic Emission Spectrometer: ICP-AES (-OES)
- e) Cold Vapor Atomic Absorption Spectrometer: CVAAS
- 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% (volume fraction)

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% nitric acid for 24 hours at room temperature, and then rinse thoroughly with 18 M-ohm ASTM Type 1 water.

- j) Volumetric flasks: Such as 25ml, 250ml, etc.
- k) Pipettes: Such as 1ml, 2ml, 5ml, 10ml, etc.
- l) Micropipettes: Such as 200µl, 500µl, 1000µl, etc
- m) Whatman filter
- n) Glass fiber filter 0.45µm (for the digestion of metals and electronics)
- o) Plastic containers for standards and digestion solutions

#### 11.5 Reagents

- a) Water: Grade 1 specified in ISO 2696:1987 used for preparation and dilution of all sample solutions
- b) Nitric acid:  $\rho(\text{HNO}_3) = 1.4\text{g/ml}$ , 65%, trace metal grade
- c) Hydrochloric acid:  $\rho(\text{HCl}) = 1.16\text{g/ml}$ , 37%, trace metal grade
- d) Potassium permanganate: G.R. 5% aqueous solution (w/v): Dissolve 5g of potassium permanganate in 100ml of reagent water
- e) Sodium chloride-hydroxylamine hydrochloride solution: Dissolve 12g of sodium chloride and 12g of hydroxylamine hydrochloride in reagent water and dilute to 100ml
- f) Tetrahydrofluoroborate solution:  $\text{HBF}_4$  50%
- g) Hydrogen peroxide:  $\text{H}_2\text{O}_2$  (30%)
- h) Sodium hydroxide: flakes: NaOH flakes
- i) Sodiumtetraboro hydrate:  $\text{NaBH}_4$
- j) Potassium borohydride, Sodium hydroxide, G.R. 1% in 0.05% NaOH: Add approximately 1000ml of reagent water to a 1L volumetric flask followed by the addition of 0.05g sodium



hydroxide. Add to 10.0g potassium borohydride and stir to dissolve. Dilute it to scale with reagent water

- k) Standard solution with 1000µg/ml of mercury

### 11.5.1 Contaminations

Contaminations can be a major source of error when working in the 10<sup>-9</sup>g range by using the instruments. Cautions handling of apparatus and careful technique will minimize this problem. The following precautions contribute to avoiding sample contamination:

- a) Use only distilled or deionized water. Care must be taken that all materials in contact with the water are composed of an inert plastic. Pure water, even when stored in PTFE, can leach impurities from the container in very short periods of time.
- 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 best to use inert plastics for sample handling.
- e) For measurements by ICP-AES(-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.

## 11.6 Sample Preparation

### 11.6.1 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 must 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 AFS, ICP-AES(-OES) and ICP/MS., the digestion solution may be analyzed straightway. By using CVAAS (cold vapor atomic absorption spectrometry) technique, the mercury is reduced to the elemental state before it is analyzed.

### 11.6.2 Wet Digestion (Digestion of metal materials and electronics)

- a) Common method for sample digestion

- Approximately 1g sample is weighed into the reaction vessel and 30ml conc. HNO<sub>3</sub> is added. The vessel is furnished with a reflux cooler and an absorption vessel containing 10ml 0.5 M HNO<sub>3</sub>, before a temperature program is started to digest the samples for 1h at room temperature and for 2h 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 250ml volumetric flask and filled up with 5 % HNO<sub>3</sub> to the mark (if the sample is digested completely).
- If the sample is not digested completely (e.g. printed wiring boards, CCFL), the sample is filtered over a 0.45µm filter and the solid residue is washed four times with 15ml 5% HNO<sub>3</sub>. The obtained solution is transferred into a 250ml volumetric flask and filled up with 5% HNO<sub>3</sub> to the mark.
- 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.

- b) Digestion of materials containing zirconium, hafnium, titanium, copper, silver, tantalum, niobium or tungsten
- Approximately 1g of the sample is weighed into a clean, dry reaction chamber and 22.5ml of concentrated HCl, 7.5ml of concentrated HNO<sub>3</sub> are added. The vessel is furnished with a reflux cooler and an absorption vessel containing 10ml 0.5 M HNO<sub>3</sub>, before a temperature program is started to digest the samples for 15 min at 95°C ± 5°C. Remove the sample from the heating digester and let it cool down to room temperature.
  - If the sample is not digested completely, repeat adding aqua regia and heat again, until the sample is digested completely. With each subsequent addition of acid, the sides of the chamber shall be rinsed so that any sample that adheres to the sides of the chamber is reintroduced into the solution.
  - When the sample is digested completely, add 20ml of reagent water and 15ml of KMnO<sub>4</sub> solution to the reaction chamber. Mix thoroughly and continue heating for 30min at 95°C ± 5°C. After cooling to room temperature the solution is quantitatively transferred over a filter into a 100ml volumetric flask. A glass rod shall be used to direct flow of solution into the funnel and to prevent dripping and/or splashing. Rinse the reaction chamber, condenser and absorber tube with the reagent water, and transfer the rinsing solution into a 250ml volumetric flask. Add 6ml of sodium chloride-hydroxylamine hydrochloride to reduce the excess permanganate. Dilute the digested sample solution to the mark with reagent water and mix thoroughly.

### 11.6.3 Microwave digestion with HNO<sub>3</sub>/HBF<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>

About 100mg of plastic material are weighed into a PTFE-TFM vessel. Five milliliters of conc. HNO<sub>3</sub>, 1.5ml 50% HBF<sub>4</sub> solution, 1.5ml 30 % H<sub>2</sub>O<sub>2</sub> 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.

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

## 11.7 Test Procedure

### 11.7.1 Standard preparation / Stock solution preparation

a) ICP-AES (OES) and AFS:

- Stock solution: Give 1ml of mercury standard solution 13.5.k (corresponding to 1000 µg Hg) into a 100ml volumetric flask; add 1 - 2 drops of potassium permanganate (5 % KMnO<sub>4</sub>) and fill up to the mark.

b) CVAAS and ICP-MS:

- Stock solution: Standard mercury solution 13.5.k
- Standard solution: Give 100µl of stock solution into a 100ml volumetric flask; add 1 - 2 drops of potassium permanganate (5% KMnO<sub>4</sub>) and fill up to the mark with 1.5% HNO<sub>3</sub>.
- Aliquots of calibration: 100µl, 200µl, 500µl
- Corresponding to: 100ng, 200ng, 500ng Hg
- Diluent: 1.5% HNO<sub>3</sub>
- Calibration volume: 10ml
- Reductant: 3% NaBH<sub>4</sub> in 1% NaOH: Dissolve NaOH flakes and NaBH<sub>4</sub> powder in deionized water and filter

NOTE: A reductant solution containing sodium borohydride in sodium hydroxid 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 inert plastic containers. The stock solution 13.5.k 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 %  $\text{KMnO}_4$  solution.

### 11.7.2 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 ( $R^2$ ) 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 must cover no more than two orders of magnitude. If the analysis results exist in the range of  $\pm 10\%$  of the real value, then the instrument is normal; otherwise repeat the analysis. If the analysis results still exceed  $\pm 10\%$  of the real value, check the instrument until the problem is solved.
- e) For CVAAS the standard calibration plot is established as follows:
  - Using suitable micro liter pipettes, 100 $\mu\text{L}$ , 200 $\mu\text{L}$  and 500 $\mu\text{L}$  of standard solution (corresponding to the weight of 100ng, 200ng and 500ng of mercury) are dispensed into 10ml 1.5%  $\text{HNO}_3$ , the measurements are done and the calibration plot is set up.

### 11.7.3 Instrument performance

NOTE: For CVAAS 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-AES, ICP-MS or AFS, the digestion solution can be determined directly.

- a) After the initial calibration, perform the instrument calibration with quality control materials. If the analysis results exist in the range of  $\pm 10\%$  of the real value, continue sample analysis; otherwise repeat the analysis. If the analysis results still exceed  $\pm 10\%$  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  $\pm 10\%$  of the real value, then the instrument is normal; otherwise repeat the analysis of the liquid standard solution. If the analysis results still exceed  $\pm 10\%$  of the real value, then recalibrate the instrument and reanalyze the previous ten samples.

### 11.7.4 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) CVAAS

- Light source: Electrodeless discharge lamp or hollow cathode lamp

- Wavelength: 253.7nm
- Spectral band width: 0.7nm
- Purge gas: N<sub>2</sub> or Ar
- Reduction agent: 3% NaBH<sub>4</sub> in 1% NaOH

b) ICP-AES

- Hg wavelength: 194.227nm;
- RF generator power: 1150w;
- Frequency: 27.12MHz;
- Argon flow Carrier gas: 0.16Mpa, Cool gas: 14L/min, Auxiliary gas: 0.5L/min;
- Sample uptake rate: 1.6ml/min.

c) ICP-MS

- Mass-charge-ratios for Hg: m/z= 199, 200, 201, 202;
- RF generator power: 1200w;
- Frequency: 27.12MHz;
- Argon flow Carrier gas: 0.28Mpa, Cool gas: 16l/min, Auxiliary gas: 1.0l/min;

d) AFS

- Source: Hg hollow cathode lamp, Current: 30mA, Wavelength: 253.7nm;
- Minus high-voltage: 360V;
- Oven temperature: 800°C;
- Argon flow carrier gas: 600ml/min, Screen gas: 1000ml/min.
- Reducing reagent: Potassium borohydride.
- Wash water: 6% HNO<sub>3</sub>

### 11.7.5 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 10% and the recovery of spiked samples should be between 90% and 110%.

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.

- a) CV-AAS: 100µl of the sample solution is given to 10ml 1.5% HNO<sub>3</sub> and the measurement is done.

### 11.7.6 Calculation of Analytical Results

The concentration measured in 11.7.5 is the concentration of mercury in the sample solution. The concentration of mercury in the sample is calculated from the equation.

a) ICP-AES

$$\text{Mercury } (\mu\text{g /g}) = (A1 - A2) V / m$$

- 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

$$\text{Mercury } (\mu\text{g /g}) = (A1 - A2) V / (1000 m)$$

- 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 (250ml for wet digestion, 25ml for microwave digestion); X, the determined weight of metal in sample aliquot in µg; A, the sample aliquot in ml (0.1ml); and m, the measured quantity of the sample in g (1g for wet digestion, 0.1g for microwave digestion).

### 11.8 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.

### 11.9 Annex (informative)

**Table 9: Program for microwave digestion of samples (power output for twelve vessels)**

Step	Time (min)	Power output (watt)	Pressure limited to (hPa)
1	5	400	35
2	5	600	35
3	12	800	35
4	20	800	40
5	3	500	40
Ventilation step	20	0	-

## 12 Determination of Lead and Cadmium in Polymer Materials by ICP-AES, 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 polymer materials from electrotechnical equipment. The document describes the use of three methods (ICP/AES, 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 samples are precut and/or milled to an appropriate size for the method selected according to the procedure describe in chapter 6. 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/AES, ICP/MS or separately by AAS.

The analysis by ICP/AES, 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 ppb level). There are some limitations: The procedure does not apply for materials containing fluorocarbons. 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 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 the annex.

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

### 12.2 References, Normative References, Reference Methods and Reference Materials

- a) EN ISO 11885:1998 Water quality – Determination of 33 elements by inductively coupled plasma atomic emission spectroscopy
- b) ISO 17294-1: Water quality- Application of inductively coupled plasma mass spectrometry (ICP-MS) for the determination of elements – Part1: General guidelines and basic
- c) EPA method 6010B:1996 Rev 2 Inductively coupled plasma-atomic spectroscopy
- d) JISK0102-54(Pb)-AAS, ICP-AES, ICP-MS
- e) JIS K0102-55(Cd)-AAS, ICP-AES, ICP-MS
- f) ISO5725 series: Accuracy (trueness and precision) of measurement methods and results
- g) JIS K 0116: General rules for atomic emission spectrometry
- h) JIS K 0133: General rules for high frequency plasma mass spectrometry
- i) ISO 3856-4: 1984: Analytical method Cd
- j) EN ISO 5961: 1995: Analytical method for Pb and Cd
- k) BCR-680 and BCR-681 (Cd and Pb in Polyethylene)
- l) VDA reference material (Cd in Polyethylene; 4 concentration levels)

### 12.3 Terms and Definitions

- a) Inductively coupled plasma atomic (optical) emission spectroscopy (ICP/AES)(-OES): Method of determining the target element contained in the sample by means of atomization and ionization of the sample with high-frequency plasma. The energy emitted

by excited atoms or ions is measured. The wavelengths of the emitted energy are specific to the elements present in the sample.

- b) Inductively coupled plasma mass spectrometry (ICP/MS): Method of determining the target element contained in the sample by means of ionizing the sample with high-frequency plasma. The generated ion is measured with mass spectrometer for the number of ions in mass-to-charge ratio ( $m/z$ ) of the target element for analysis of the element or its isotope.
- c) Atomic absorption spectrometry (AAS): Method of determining the target element contained in the sample by means of nebulizing and exciting the sample with an air-acetylene flame and measuring the absorption of the atomic absorption lines obtained.
- d) Spectral interferences: Interference that results in case of (ICP/AES (-OES) or AAS) from overlapping optical spectrum caused by atoms or ions with spectral lines close to the spectral line of the target element; or in case of (ICP/MS)) from overlapping mass spectrum caused by atoms or polyatomic ion with mass-to-charge ratio ( $m/z$ ) close to the  $m/z$  of the target element.
- e) Memory effect: Phenomenon caused by presence of elements in sample or standard calibration solution analyzed previously in the high-frequency plasma spectrometer or accompanying device, causing partial overlap with target element spectral signal in the current analyte.
- f) Test sample solution: Sample prepared for measurement.
- g) Calibration standard: Solution containing existing concentration of method analytes for developing a calibration curve.
- h) Calibration blank: Solution identical in composition as a calibration standard without content of method analytes.
- i) Internal standard element: Elements added in identical concentrations in calibration standard, calibration blank and sample solution, in order to adjust non-spectral interference and time-series change in the sensitivities of the used analytical equipment.
- j) Laboratory reagent blank: An aliquot of reagent water or other blank matrix that is treated exactly as a sample to determine contamination of laboratory, equipment and reagents by method analytes or other interferences, including contact with glassware and other equipment used in analysis and addition of solvent, reagent, and in internal standard element.
- k) Instrument reading: in case of (ICP/AES(-OES) and AAS) emission intensities are proportional to the concentration of the target element or in case of (ICP/MS)) ionic current or proportionate value in mass-to-charge ratio of the target element.
- l) Detection limit: Concentration able to produce triple the standard deviation for the intensities of either the atomic spectra lines (ICP/AES (-OES) and AAS) or the intensities of the selected mass-to-charge ratios (ICP/MS) or background intensity when calibration blank is measured 10 times in succession.
- m) Resolution: The capability of a spectrometer to separate two spectral lines in close proximity with each other.
- n) Quality control: Procedure to guarantee that analysis has been conducted precisely in compliance with specified standards, in order to assure data reliability.

## 12.4 Apparatus/Equipment and Materials

### 12.4.1 Apparatus/Equipment

- a) ICP/AES(-OES): Equipment consisting of sample holder, plasma torch, 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% (volume fraction)
  - f) Acetylene gas: Gas with purity of over 99.99% (volume fraction)
  - g) Scale: Precision level of 0.1mg
  - h) Glassware: All glassware shall be cleaned with 10% volume fraction nitric acid before use
    - Kjeldhal flask: 100ml
    - Beakers: such as 100ml, 200ml, etc.
    - Volumetric flasks: Such as 50ml, 100ml, 200ml etc.
    - Pipettes: Such as 1ml, 5ml, 10ml, 20ml, etc.
    - Funnel
    - Watch glass
    - Crucible: Such as 50ml, 150ml, etc.
  - i) Crucible, of platinum: Such as 50ml, 150ml, etc.
  - j) Crucible, of porcelain: Such as 50ml, 150ml, etc.
  - k) PTFE/PFA equipment Poly(tetrafluoroethylene) (PTFE) / Perfluoroalkoxy (PFA): All equipment shall be cleaned with 10% volume fraction nitric acid before use
    - Beakers: Such as 100ml, 200ml, etc.
    - Volumetric flasks: Such as 100ml, 200ml, 500ml, etc.
  - l) Micropipettes: Such as 10 $\mu$ l, 100 $\mu$ l, 200 $\mu$ l, 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 must confirm the suitability of the container selected.
  - n) Electric hot plate or heated sand bath
  - o) Muffle furnace: capable of being maintained 450  $\pm$  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) Microwave digestion vessel: Such as 100ml, etc.
  - s) Heat resistant thermal insulation board
  - t) Paper filter

## 12.5 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.

- a) Water: Grade 1 specified in ISO 3696:1987 used for preparation and dilution of all sample solutions.
- b) Sulfuric acid:  $\rho(\text{H}_2\text{SO}_4) = 1.84\text{g/ml}$ , 95%
- c) Nitric acid:  $\rho(\text{HNO}_3) = 1.40\text{g/ml}$ , 65%
- d) Hydrogen-peroxide:  $\rho(\text{H}_2\text{O}_2) = 1.10\text{g/ml}$ , 30%
- e) Hydrochloric acid:  $\rho(\text{HCl}) = 1.19\text{g/ml}$ , 37%



- f) Hydrofluoric acid:  $\rho(\text{HF}) = \text{ISO } 40 \approx 42\%$  ;  $\text{JIS } 46 \approx 48\%$
- g) Boric acid ( $\text{HBO}_3$ )
- h) Standard solution with  $1000\mu\text{g/l}$  of lead
- i) Standard solution with  $1000\mu\text{g/l}$  of cadmium
- j) 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 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/AES(-OES), Sc or Y is recommended, for the use with ICP/MS, Rh is recommended. The concentration used should be  $1000\mu\text{g/l}$ .

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

NOTE: Special precaution measures should be taken in case that hydrofluoric acid is used.

## 12.6 Sample Preparation

### 12.6.1 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 wet acid digestion  $400\text{mg}$  of sample that has been ground, milled or cut is measured accurately to the  $0.1\text{mg}$  level. For the dry ashing method or for the closed system for acid decomposition  $200\text{mg}$  of sample that has been ground, milled or cut is measured accurately to the  $0.1\text{mg}$  level.

### 12.6.2 Preparation of test solution

#### 12.6.2.1 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  $450 \pm 25^\circ\text{C}$ , 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.  $5\text{ml}$  of nitric acid are added, and the resulting solution is transferred to a  $50\text{ml}$  volumetric flask and filled up with water to  $50\text{ml}$ . 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  $50\text{ml}$ , internal standard of  $500\mu\text{l}$  for ICP-AES, and  $500\text{nl}$  for ICP-MS, respectively, has to be added before filling up.

- b) When sample contains halogen compounds (information may be available from previous screening experiments)
- The sample is measured into a crucible. 10 to 15ml 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. 5ml 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  $450 \pm 25^{\circ}\text{C}$  and the sample is evaporated, dried, and ashed until the carbon has been completely incinerated. After ashing, 5ml 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 50ml, internal standard of 500 $\mu\text{l}$  for ICP-AES, and 500nl 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 Chapter 12.1.

#### 12.6.2.2 Wet 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. 5ml of sulfuric acid and 1ml 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. 0.5ml), 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 100ml volumetric flask and the flask is then filled with water to 100ml. 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 100ml, internal standard of 1000 $\mu\text{l}$  for ICP-AES, and 1000nl for ICP-MS, respectively, has to be added before filling up.
- c) When general digestion is inadequate or when the sample contains silica, titanium, etc. (information may be available from previous screening):
- The sample is measured into a flask. 5ml of sulfuric acid and 1ml 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. 0.5ml), 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. 5ml 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 100ml volumetric flask and the flask is then filled with water to 100ml. 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

100ml, internal standard (12.5 j) of 1000 $\mu$ l for ICP-AES, and 1000nl 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.

#### 12.6.2.3 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 1ml) 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 50ml volumetric flask and the flask is then filled 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 50ml, internal standard of 500 $\mu$ l for ICP-AES, and 500nl for ICP-MS, respectively has to be added before filling up.

NOTE: 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 silica, titanium, etc. (Information may be available from previous screening):

- The sample is measured into a microwave digestion vessel. 5ml of nitric acid and 1ml of hydrofluoric acid are added. The addition of hydrogen peroxide in small or catalytic quantities (such as 0.1 to 1ml) 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 50ml volumetric flask and the flask is then filled 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 50ml, internal standard of 500 $\mu$ l for ICP-AES, and 500nl for ICP-MS, respectively has to be added before filling up.

NOTE: 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.

#### 12.6.3 Preparation of laboratory reagent blank

Procedure identical to sample preparation is executed concurrently without sample.

### 12.7 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.

#### 12.7.1 Preparation of calibration solution

Calibration blank and three calibration standards are prepared as calibration solutions.

After diluting each standard element solution gradually, the diluted standard solutions containing 0-100µg of each element are transferred to a 100ml 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.

### 12.7.2 Development of calibration curve

The spectrometers are prepared for quantification. Some of the solution obtained in 12.7.1 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/AES(-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 chapter 12.9, table 10.

#### 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 chapter 12.9, table 11.

#### 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 chapter 12.9, table 12. 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.

### 12.7.3 Measurement of sample

After development of the calibration curve, the laboratory reagent blank and the sample solution are measured. If the sample concentration is higher than the concentration curve, the solution must be diluted to the range of the calibration curve 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.

### 12.7.4 Calculation

The concentration measured in 12.7.3 is the concentration of each element in the sample solution. The concentration of each element in the sample is calculated from the equation:

$$\text{Cadmium or Lead } (\mu\text{g /g}) = (A1 - A2) \times V / m$$

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.

### 12.8 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.

### 12.9 Annex (informative)

#### 12.9.1 ICP/AES(-OES)

**Table 10: Spectral interferences for the wavelengths of cadmium and lead**

	Cd	Cd	Cd	Cd	Pb	Pb	Pb	Pb
(nm)	214,439	226,502	228,802	361,051	217,000	220,353	261,417	283,305
Ag	+	+	+	+	+	+	+	+
As	++	+	+++	+	+	+	+	+
Au	+	+	++	+	+	+	+	+++
B	+	+	+	+++	+	+	++	+
Ca	+	+	+	+	+	+	+	+
Co	+	++	+++	+++	++	+++	+++	++
Cr	+	+	+	+	+	+	++	+
Cu	+	+	+	+	+	+	+	++
Eu	+	+	+	+++	++	+	+++	+++
Ga	+	+	+	+	+	+	+	+
Ge	+	+	+	+	+	+	+	+
In	+	+	+	+	+	+	+	+
Ir	++	++	++	++	+++	+++	+++	+++
Mg	+	+	+	+	+	+	+	++
Mn	+	+	+	+++	+	++	+++	+
Mo	++	+	+	+++	++	+	++	+++
Ni	+	+	++	+++	+++	++	+	+
Pd	+	+	+	+	+	+++	+	+
Pt	+++	+	++	+	+	+	+	+
Re	++	++	+	+++	++	+++	++	+++
Ru	++	+	++	+	++	+	+++	+
Sb	++	+	+	+	++	+	+	+
Sc	+	+	+++	++	++	++	+++	++
Sn	+	+	+	+	++	+	+	++

V	+	+	++	+++	++	++	++	+
W	++	++	++	++	+++	+	+++	++
Zn	+	+	+	+	+++	+	+	+
Al	+	+	+	+	+++	+++	+	++
Ti	+	+	+	++	+	+++	+	++
Fe	+++	+++	+	++	+++	++	+++	+++
Nb	+	+	+	-	-	+	-	+++
Hf	-	-	-	-	-	+	-	+++
Ta	-	-	-	-	-	+	-	++
Pb	+	+	+	+	-	-	-	-
Cd	-	-	-	-	+	+	+	+

The table shows the strength of interference for the wavelengths of Cd and Pb when 1000 ppm of the corresponding matrix elements are introduced

- + no or small interference (typical less than 0.05ppm)
- ++ medium interference (typical between 0.05 ppm and 0.2 ppm)
- +++ strong interference (typical more than 0.2 ppm)

### 12.9.2 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 must be paid to positive interference in cadmium mass measurement.

**Table 11: Examples for mass-charge-ratios**

Element	Isotope	Isobar	Polyatomic ion
Cd	111Cd		MoO, MoOH, ZrOH
	112Cd	Sn	MoO, MoOH
	113Cd	In	MoO, MoOH, ZrOH, RuO
	114Cd	Sn	MoO, MoOH, RuO
Pb	204Pb		
	206Pb		PtO
	207Pb		IrO
	208Pb		PtO

### 12.9.3 AAS

Recommended measurement wavelengths for AAS

**Table 12: Examples for wavelengths for AAS**

Element	Wavelength / nm	Slit width / nm
Cd	228.8	0.7
Pb	261.4	0.7
	217.0	0.7
	283.3	0.7

Light source: Electrodeless discharge lamp or hollow cathode lamp, Gas type: Acetylene/Air

## **13 Determination of Lead and Cadmium in Metallic Materials by ICP-AES, 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 metallic materials from electrotechnical equipment. The document describes the use of three methods (ICP/AES, 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/AES (-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 analysis by ICP/AES, 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 ppb level). The particular precision and the detection limits of the different methods depend on the equipment and on the individual sample/procedure as well. Typical data are given including the most probable occurring interferences in order to support the experts to select the most appropriate analytical procedure.

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 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.

### **13.2 References, Normative References, Reference Methods and Reference Materials**

- a) ISO5725 series: Accuracy (trueness and precision) of measurement methods and results
- b) ISO 11885: 1996: Inductively Coupled Plasma Atomic(Optical) Emission Spectroscopy
- c) ISO 17294-1: Water quality- Application of inductively coupled plasma mass spectrometry (ICP-MS) for the determination of elements – Part1: General guidelines and basic
- d) JIS K 0116: General rules for atomic emission spectrometry
- e) JIS K 0133: General rules for high frequency plasma mass spectrometry
- f) ISO 3856-4: 1984: Analytical method Cd
- g) EN ISO 5961: 1995: Analytical method for Pb and Cd
- h) ISO 3696:1987 – specification of water
- i) ISO 40 and JIS 40 – specification of hydrofluoric acid

### **13.3 Terms and Definitions**

- a) Inductively coupled plasma atomic emission spectrometry (ICP/AES(-OES)): Method of determining the target element contained in the sample by means of nebulizing and exciting the sample with inductively coupled plasma and measuring the intensities of the atomic spectra lines obtained.
- b) Inductively coupled plasma mass spectrometry (ICP/MS): Method of determining the target element contained in the sample by means of ionizing the sample with high-frequency plasma. The generated ion is measured with mass spectrometer for the number of ions in the mass-to-charge ratio (m/z) of the target element for analysis of the element or its isotope.

- c) Atomic absorption spectrometry (AAS): Method of determining the target element contained in the sample by means of nebulizing and exciting the sample with an air-acetylene flame and measuring the absorption of the atomic absorption lines obtained.
- d) Test sample solution: The solution prepared with the fraction of the test sample according to the appropriate specifications, such that it can be used for the envisaged measurement.
- e) Analyte: element(s) to be determined
- f) Calibration standard: Solution containing known concentration of analyte for developing a calibration curve.
- g) Calibration blank: Solution identical in composition as a calibration standard with zero concentration of analyte.
- h) Internal standard element: Elements added in identical concentrations to calibration standard, to calibration blank and to sample solution, in order to adjust optical or mass-to-charge ratio interferences and time-series changes in the sensitivity of the used analytical equipment (ICP/AES (-OES), ICP/ MS, AAS).
- i) Laboratory reagent blank: An aliquot of reagent water or other blank matrix that is treated exactly as a sample in order to determine contamination of laboratory, equipment and reagents by analyte or other interference, including contact with glassware and other equipment used in analysis and addition of solvent, reagent, and in internal standard element.
- j) Detection limit: Concentration able to produce triple the standard deviation for the intensities of either the atomic spectra lines (ICP/AES (-OES) and AAS) or the intensities of the selected mass-to-charge ratios (ICP/MS) or background intensity when calibration blank is measured 10 times in succession.
- k) Resolution: The capability of a spectrometer to separate two spectral lines in close proximity with each other.
- l) Memory effect: Phenomenon caused by presence of elements in sample or standard calibration solution analyzed previously in the high-frequency plasma spectrometer or accompanying device, causing partial overlap with target element spectral signal in the current analyte.
- m) Quality control: Procedure to guarantee that analysis has been conducted precisely in compliance with specified standards, in order to assure data reliability.

#### 13.4 Apparatus/Equipment and Materials

- a) Scale: Precision level of 0.1mg
- b) Glassware: All glassware shall be cleaned with 10% volume fraction nitric acid before use
  - Beakers: Such as 100ml, 200ml, 500ml, etc.
  - Volumetric flasks: Such as 100ml, 200ml, 500ml, etc.
  - Pipettes: Such as 1ml, 5ml, 10ml, 20ml, etc.
  - Watch glass
- c) Micropipettes: Such as 200µl, 500µl, 1000µl, etc.
- d) Poly(tetrafluoroethylene) (PTFE) / Perfluoroalkoxy (PFA) equipment: All equipment shall be cleaned with 10% volume fraction nitric acid before use
  - Beaker: Such as 100ml, 200ml, 500ml, etc.
  - Watch glass
  - Volumetric flasks: Such as 100ml, 200ml, 500ml, etc.
- e) Volumetric flasks made of high-density polyethylene: Such as 100ml, 200ml, 500ml, etc.
- 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/AES(-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, 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% (volume fraction)
- m) Acetylene gas: Gas with purity of over 99.99% (volume fraction)

### 13.5 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.

- a) Water: Grade 1 specified in ISO 3696:1987 used for preparation and dilution of all sample solutions.
- b) Hydrochloric acid:  $\rho(\text{HCl}) = 1.16\text{g/ml}$
- c) Nitric acid:  $\rho(\text{HNO}_3) = 1.4\text{g/ml}$
- d) Nitric acid: Dilution (1+ 2): Dilute 1 volume of concentrated nitric acid (13.5 c) with 2 volumes of water (13.5 a).
- e) Perchloric acid:  $\rho(\text{HClO}_4) = 1.67\text{g/ml}$ , 70%
- f) Phosphoric acid:  $\rho(\text{H}_3\text{PO}_4) = 1.69\text{g/ml}$ , more than 85%
- g) Sulfuric acid:  $\rho(\text{H}_2\text{SO}_4) = 1.84\text{g/ml}$
- h) Sulfuric acid: Dilution (1+1): Dilute 1 volume of concentrated sulfuric acid (13.5. g) with 2 volumes of water (13. 5 a).
- i) Hydrofluoric acid:  $\rho(\text{HF}) = \text{ISO } 40\sim 42\%$ 、 $\text{JIS } 46\sim 48\%$
- j) Hydrobromic acid:  $\rho(\text{HBr}) = 1.48\text{g/ml}$ , 47~49%
- 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 $\mu\text{g/l}$  of lead
- o) Standard solution with 1000 $\mu\text{g/l}$  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 must be at negligible levels. Sc, In, Tb, Lu, Re, Rh, Bi and Y may be used as internal standard elements.

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

NOTE: Special precaution measures should be taken in case that hydrofluoric acid or perchloric acid (requires special hood, risk of explosion) is used.

## 13.6 Sample Preparation

### 13.6.1 Test portion

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

### 13.6.2 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. 20ml 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 100ml volumetric flask and the flask then filled with water to 100ml. 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 with a watch glass. 20ml 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 watch glass and inside wall of the beaker are rinsed with water, and the watch glass is removed. The solution is transferred to a 100ml volumetric flask and the flask is filled with water to 100ml. 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 with a watch glass. 10ml 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 watch glass and inside wall of the beaker are rinsed with water, and the watch glass is removed. 10ml

of sulfuric acid is added and the beaker is heated until white fumes of  $\text{SO}_3$  are liberated. After cooling for several minutes, 20ml 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 100ml volumetric flask which is then filled with water to 100ml. 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.

- Alternatively 1 gram of sample is to be dissolved by the addition of 40ml of water, 12ml of concentrated nitric acid, and 6ml of freshly prepared fluoroboric acid (200ml of 40% hydrofluoric acid with 75g of boric acid).

NOTE: If containing a large quantity of tin, the dissolving acid should be selected carefully to prevent undissolved precipitation. Otherwise tin should be deleted from the sample solution.

### 13.6.3 Preparation of laboratory reagent blank

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

## 13.7 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: 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: 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.

### 13.7.1 Preparation of calibration standard

#### a) Calibration method (Matrix matching method)

- Calibration blank and three calibration standards are prepared as calibration solutions.
- After diluting each standard element solution gradually, the diluted standard solutions containing 0 – 100 $\mu\text{g}$  of each element are transferred to a 100ml volumetric flask. 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 EDXRF. 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

- Calibration blank and three calibration standards are prepared as calibration solutions.
- Each standard element solution is added in steps in 100ml 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.

### 13.7.2 Measurement of calibration standard

#### a) ICP/AES(-OES)

- Some part of the calibration solutions prepared as described in 13.7.1 is introduced into the argon plasma in ICP-AES 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 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 chapter 13.9, table 13. 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 13.7.1 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 14.

#### c) AAS

- Portions of the calibration solutions prepared as described in 13.7.1 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 15. 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.

### 13.7.3 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 must 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.

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.

### 13.7.4 Calculation

The spectrometer readings of each sample as obtained according to 13.7.3 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:

$$\text{Cadmium or Lead } (\mu\text{g /g}) = (A1 - A2) V / m$$

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.

### 13.8 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.

### 13.9 Annex (informative)

#### 13.9.1 ICP/AES(-OES)

**Table 13: Spectral interferences for the wavelengths of cadmium and lead**

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

Hf	-	-	-	-	-	+	-	+++
Ta	-	-	-	-	-	+	-	++
Pb	+	+	+	+	-	-	-	-
Cd	-	-	-	-	+	+	+	+

The table shows the strength of interference for the wavelengths of Cd and Pb when 1000 ppm of the corresponding matrix elements are introduced

- + no or small interference (typical less than 0.05ppm)
- ++ medium interference (typical between 0.05 ppm and 0.2 ppm)
- +++ strong interference (typical more than 0.2 ppm)

### 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 2 shows one example of the effect of background correction. Figure 2(a) shows the example of uniform background versus wavelength. In this case, background could be corrected by both of position A and B. Figure 2(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.

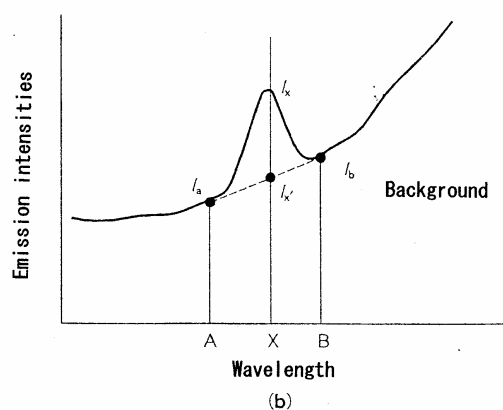
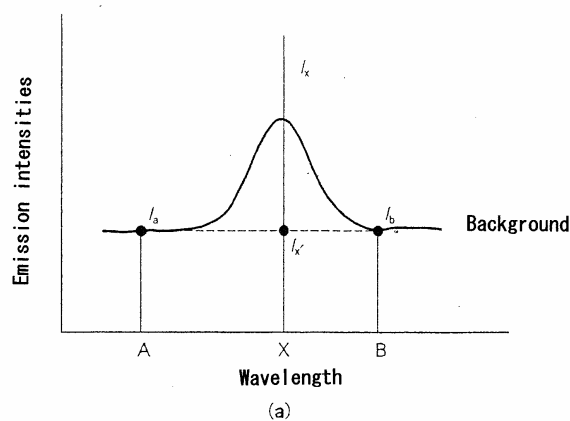


Figure 2: Background Correction

### 13.9.2 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 must be paid to positive interference in cadmium mass measurement.

**Table 14: Examples for mass-charge-ratios**

Element	Isotope	Isobar	Polyatomic ion
Cd	111Cd		MoO, MoOH, ZrOH
	112Cd	Sn	MoO, MoOH
	113Cd	In	MoO, MoOH, ZrOH, RuO
	114Cd	Sn	MoO, MoOH, RuO
Pb	204Pb		
	206Pb		PtO
	207Pb		IrO
	208Pb		PtO

### 13.9.3 AAS

Recommended measurement wavelengths for AAS.

**Table 15: Examples for wavelengths for AAS**

Element	Wavelength /nm	Slit width / nm
Cd	228.8	0.7
Pb	261.4	0.7
	217.0	0.7
	283.3	0.7

## **14 Determination of Lead and Cadmium in Electronics by ICP-AES, ICP-MS, and AAS**

### **14.1 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/AES, 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 chapter 5. The powder is either digested with aqua regia or microwave-enhanced with HNO<sub>3</sub>, HBF<sub>4</sub>, H<sub>2</sub>O<sub>2</sub> 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/AES(-OES) or by ICP/MS or one element after the other by AAS.

The analysis by ICP/AES, 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 ppb level). These advantages may be limited, when the samples to be analyzed have a highly complex composition. The electronics must 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 (not topic of this standard). 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 by the use of different analytical means that no target elements are included in these 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 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.

### **14.2 References, Normative References, Reference Methods and Reference Materials**

- a) DIN EN ISO 5961; former DIN 38.414, part 7 Sludge and Sediment (Group S)
- b) Edgell, K.; US EPA Method Study 37 - SW-846 Method 3050 Acid Digestion of Sediments, Sludges, and Soils. EPA Contract No. 68-03-3254, November 1988
- c) Kimbrough, David E., and Wakakuwa, Janice R. Acid Digestion for Sediments, Sludges, Soils, and Solid Wastes. A Proposed Alternative to EPA SW 846 Method 3050, Environmental Science and Technology, Vol. 23, Page 898, July 1989
- d) T. Ernst, R. Popp, M. Wolf, R. van Eldik, Analysis of eco-relevant elements and noble metals in printed wiring boards using AAS, ICP-AES and EDXRF, Anal. Bioanal. Chem. (2003) 375 : 805-814
- e) ISO 17294-1: Water quality- Application of inductively coupled plasma mass spectrometry (ICP-MS) for the determination of elements – Part1: General guidelines and basic ISO5725: series Accuracy (Trueness and precision) of measurement methods and results
- f) JIS K 0133: General rules for high frequency plasma mass spectrometry
- g) EN ISO 5961: 1995: Analytical method for Pb and Cd
- h) ISO 3856-4: 1984: Analytical method Cd
- i) Certified Reference Materials (CRMs) for Electronics (PCBs/Components) are not available.



### 14.3 Terms and Definitions

- a) Inductively coupled plasma atomic (optical) emission spectroscopy (ICP/AES(-OES)): Method of determining the target element contained in the sample by means of atomization and ionization of the sample with high-frequency plasma. The energy emitted by excited atoms or ions is measured. The wavelengths of the emitted energy are specific to the elements present in the sample.
- b) Inductively coupled plasma mass spectrometry (ICP/MS): Method of determining the target element contained in the sample by means of ionizing the sample with high-frequency plasma. The generated ion is measured with mass spectrometer for the number of ions in mass-to-charge ratio ( $m/z$ ) of the target element for analysis of the element or its isotope.
- c) Atomic absorption spectrometry (AAS): Method of determining the target element contained in the sample by means of nebulizing and exciting the sample with an air-acetylene flame and measuring the absorption of the atomic absorption lines obtained.
- d) Spectral interferences: Interference that results from overlapping mass spectrum caused by atoms or polyatomic ion with mass-to-charge ratio ( $m/z$ ) close to the  $m/z$  of the target element.
- e) Memory effect: Phenomenon caused by presence of elements in sample or standard calibration solution analyzed previously in the high-frequency plasma spectrometer or accompanying device, causing partial overlap with target element spectral signal in the current analyte.
- f) Analytical sample: Sample prepared for measurement.
- g) Calibration standard: Solution containing existing concentration of method analytes for developing a calibration curve.
- h) Calibration blank: Solution identical in composition as a calibration standard with zero concentration of method analytes.
- i) Internal standard element: Elements added in identical concentrations in calibration standard, calibration blank and sample solution, in order to adjust non-spectral interference and time-series change in sensitivity in high-frequency plasma mass spectrometer.
- j) Laboratory reagent blank: An aliquot of reagent water or other blank matrix that is treated exactly as a sample to determine contamination of laboratory, equipment and reagents by method analytes or other interferences, including contact with glassware and other equipment used in analysis and addition of solvent, reagent, and in internal standard element.
- k) Instrument reading: Ionic current or proportionate value in mass-to-charge ratio of the target element
- l) Detection limit: Concentration able to produce triple the standard deviation for luminescence intensity or background intensity when calibration blank is measured 10 times in succession.
- m) Quality control: Procedure to guarantee that analysis has been conducted precisely in compliance with specified standards, in order to assure data reliability.
- n) Matrix matching of standards: The attempt to simulate the sample matrix as closely as possible in the calibration standards.
- o) PCB: Printed circuit board (synonymous: PWB – printed wiring board).

### 14.4 Apparatus / Equipment and Materials

- a) ICP/AES(-OES): Inductively Coupled Plasma Atomic (Optic) Emission Spectrometer, ICP-AES(-OES), equipped with sequential optic or with polychromators.
- b) ICP/MS: Inductively Coupled Mass Spectrometer (ICP/MS), 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% (volume fraction)
- 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% (volume fraction)
- 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) Micro wave 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 0.1mg
- j) Glassware: All glassware shall be cleaned with 10% volume fraction nitric acid before use
  - Beakers: Such as 100ml, 200ml, 500ml, etc.
  - Volumetric flasks: Such as 100ml, 200ml, 500ml, etc
  - Pipette: Such as 1ml, 5ml, 10ml, 20ml, etc.
  - Graduated cylinder
  - Watch glass
- k) Micropipette: Such as 200 $\mu$ l, 500 $\mu$ l, 1000 $\mu$ l, etc.
- l) PTFE/PFA containers: All equipment shall be cleaned with 10% volume fraction nitric acid before use
  - Beakers: Such as 100ml, 200ml, 500ml, etc.
  - Volumetric flasks: Such as 100ml, 200ml, 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 must confirm the suitability of the container selected.
- n) Electric hot plate or heated sand bath
- o) Microwave digestion vessel: Such as 40ml, 100ml, etc.
- p) Filter:
  - Glass fiber filter 0.45 $\mu$ m (digestion with aqua regia)
  - Whatman filter 0.45 $\mu$ m (microwave digestion)

#### 14.5 Reagents

- a) Water: Grade 1 specified in ISO 3696:1987 used for preparation and dilution of all sample solutions
- b) Hydrochloric acid:  $\rho(\text{HCl}) = 1.16\text{g/ml}$ , 37 %
- c) Hydrochloric acid: Dilution (1+ 5): One part hydrochloric acid (14.5 b) diluted with two parts water (14.5 a).
- d) Nitric acid:  $\rho(\text{HNO}_3) = 1.4\text{g/ml}$ , 65%
- e) Mixed acid (3 parts hydrochloric acid and 1 part nitric acid)
- f) Tetrafluoroborate solution,  $\text{HBF}_4$ , 40%
- g) Hydrogen peroxide  $\text{H}_2\text{O}_2$ , 30%, p.a. grade

- h) Standard solution with 1000µg/g of lead
- i) Standard solution with 1000µg/g of cadmium
- j) Standard solution with 10000µg/g of copper
- k) Standard solution with 10000µg/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 must 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: 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: 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: 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: The exhaust gases from the plasma should be ducted away by an efficient fume extraction system.

NOTE: Special precaution measures should be taken in case that hydrofluoric acid or perchloric acid (requires special hood, risk of explosion) is used.

## 14.6 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 losing 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.

### 14.6.1 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 must 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/AES or AAS or can be diluted for the use in ICP/MS.

### 14.6.2 Digestion with aqua regia

Approximately 2g of the ground sample (maximum grain size: 250µm) is weighed into the reaction vessel and 22.5ml conc. HCl and 7.5ml conc. HNO<sub>3</sub> are added. The vessel is furnished with a reflux cooler and an absorption vessel containing 10ml 0.5 M HNO<sub>3</sub>, 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 0.45µm filter and the solid residue is washed

four times with 15ml 5% HCl. The obtained solution is transferred into a 250ml volumetric flask and filled up with 5% 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 100ml, internal standard of 1000µl for ICP-AES, and 1000nl 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. EDXRF) 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 HNO<sub>3</sub>) 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.

### 14.6.3 Microwave digestion

300mg of ground sample (maximum grain size: 250µm) is weighed into a PTFE-TFE or a PTFE/PFA vessel. 4ml of nitric acid, 2ml of tetrafluoroborate, 1ml of hydrogen peroxide and 1ml of water are added. The vessels are agitated carefully for approximately 10s 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 poly(vinyl chloride) and in addition some of the metal elements are dissolved.

The vessel is opened after cooling to room temperature (approximately required time: 1h), and 4ml conc. HCl 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 chapter 14.9 (Table 16).

After cooling the vessel to room temperature again (approximately required time: 1h), it is opened and the solution is filtered over a Whatman filter into a 25ml flask, washed and filled to the mark with 5% 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 appreciated, if more than one simultaneous runs are performed.

NOTE: It is highly recommended not to weigh in more than 300mg 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 (CO<sub>2</sub>, NO<sub>x</sub>, 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: Also weigh in same sample amounts and same type of samples when you analyze more than one sample in simultaneously in one run!

If a sample amount of more than 300mg 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 1.2g is needed. Therefore 4 x 300mg 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 (0.45µm) into a 100ml volumetric flask, washed and filled to the mark with 5% HCl.

## 14.7 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-AES and AAS. The internal standard method (intensity comparison method) is recommended for ICP-MS.

NOTE: To increase the reliability of the test method, the standard-additions method may be used.

NOTE: 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.

### 14.7.1 Preparation of calibration solution

#### a) Calibration method (Matrix matching method)

- Calibration blank and three calibration standards are prepared as calibration solutions.
- After diluting each standard element solution gradually, the diluted standard solutions containing 0 - 100µg of each element are transferred to a 100ml volumetric flask. 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

- Calibration blank and three calibration standards are prepared as calibration solutions.
- Each standard element solution is added in steps in 100ml 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/AES, AAS: The high iron and copper content necessitates a close matrix matching of standard solutions and an appropriate line selection (Reference 14.2 d). Therefore the calibration should be done using matrix adjusted calibration solutions. Recommended wavelengths can be found in chapter 14.9.

d) ICP/MS: Here the use of an appropriate internal standard is recommended. Chapter 14.9 gives the best m/z for the measurements together with potential interferences.

### 14.7.2 Standard preparation

#### a) ICP/AES, 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/AES 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: 10% HCl
  - Calibration standards 1 to 3 (100ml in each case): Solutions containing 1500µg/ml Fe and 1500µg/ml Cu, 24ml HCl 37% and target elements Pb and Cd in different concentrations. 1.0µg/ml target element in solution corresponds to 125µg/g target element in electronics.
- c) Microwave digestion standards
- Calibration blank: Mixture of 92ml 10% HCl and 8ml HBF<sub>4</sub> 50%
  - Calibration standards 1 to 3 (100ml in each case): containing 1500mg/l Fe and 1500µg/ml Cu, 24ml HCl 37%, 8ml HBF<sub>4</sub> and Pb and Cd in different concentrations. 1.2µg/ml target element in solution corresponds to 100µg/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 100ml measuring flasks with 0-5µg of each element. Next, each reagent and 1µg of rhodium solvent are added to achieve reagent concentrations identical to that of the sample solution, and mixed calibration standard solution is prepared.

### 14.7.3 Calibration

a) ICP/AES, AAS

- The calibration blank and standard solutions are measured by ICP/AES 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 14.7.1 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.

### 14.7.4 Development of calibration curve

a) ICP/AES(-OES)

- Some part of the calibration solutions prepared as described in 14.7.1 is introduced into the argon plasma in ICP-AES 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 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 17. 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 14.7.1 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 chapter 14.9, Table 18.

#### c) AAS

- Portions of the calibration solutions prepared as described in 14.7.1 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 chapter 14.9 (Table 19). 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.

#### 14.7.5 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 must 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.

#### 14.7.6 Calculation of Analytical Results

The spectrometer readings of each sample as obtained according to 14.7.3 and the calibration curve developed as described in 14.7.2 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:

$$\text{Lead or cadmium } \mu\text{g /g} = (A1 - A2) V / m \quad (\text{Eq. 1})^*$$

where A1 is concentration of each target element in the test sample solution in  $\mu\text{g/ml}$ ; A2, the concentration of each target element in the laboratory reagent blank in  $\mu\text{g/ml}$ ; V the volume of the concentrate sample solution in ml; and m, the measured mass of sample in g.

\* 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.

#### 14.8 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.

#### 14.9 Annex (informative)

**Table 16: Program for microwave digestion of samples (power output for five vessels)**

Step	Time (min)	Power output (watt)	Pressure limited to (hPa)
1A	5	300	25
2A	5	350	25
3A	17	450	25

4A	2	300	25
Ventilation step A	3	0	25
1B	5	300	25
2B	5	400	25
3B	17	450	25
Ventilation step B	3	0	25

#### 14.9.1 ICP/AES(-OES)

**Table 17: Recommended wavelengths and interfering elements (Spectral interferences for the wavelengths of cadmium and lead)**

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



Pb	+	+	+	+	-	-	-	-
Cd	-	-	-	-	+	+	+	+

The table shows the strength of interference for the wavelengths of Cd and Pb when 1000 ppm of the corresponding matrix elements are introduced

+ no or small interference (typical less than 0.05ppm)  
 ++ medium interference (typical between 0.05 ppm and 0.2 ppm)  
 +++ strong interference (typical more than 0.2 ppm)

### 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 3 shows one example of the effect of background correction. Figure 3(a) shows the example of uniform background versus wavelength. In this case, background could be corrected by both of position A and B. Figure 3(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.

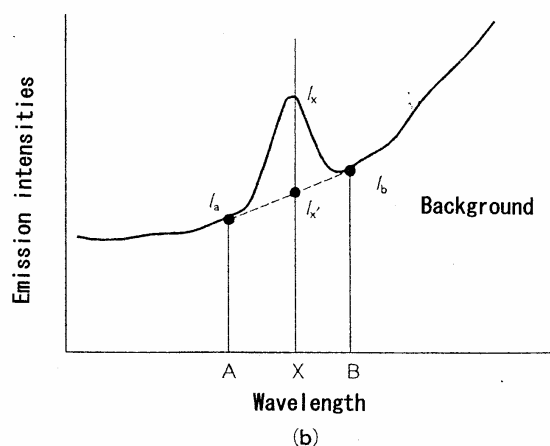
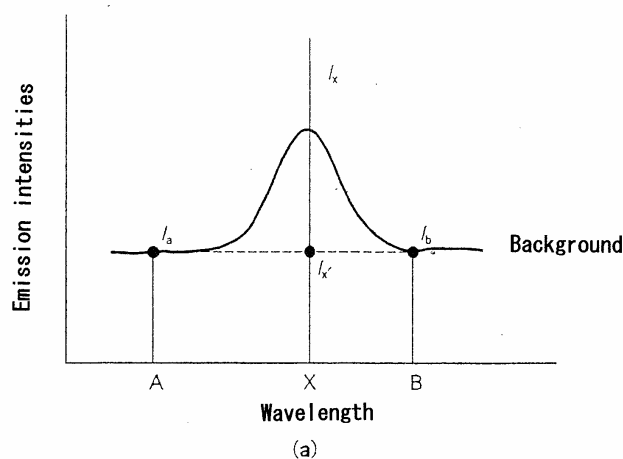


Figure 3: Background Correction

### 14.9.2 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 must be paid to positive interference in cadmium mass measurement.

**Table 18: Examples for mass-charge-ratios**

Element	Isotope	Isobar	Polyatomic ion
Cd	111Cd		MoO, MoOH, ZrOH
	112Cd	Sn	MoO, MoOH
	113Cd	In	MoO, MoOH, ZrOH, RuO
	114Cd	Sn	MoO, MoOH, RuO
Pb	204Pb		
	206Pb		PtO
	207Pb		IrO
	208Pb		PtO

### 14.9.3 AAS

Recommended measurement wavelengths for AAS

**Table 19: Examples for wavelengths for AAS**

Element	Wavelength /nm	Slit width / nm
Cd	228.8	0.7
Pb	261.4	0.7
	217.0	0.7
	283.3	0.7

Gas type: Acetylene/Air

Light source: Electrodeless discharge lamp or hollow cathode lamp

## 15 Reference Methods and Materials

Reference Material Standards (RMS) are indispensable to obtain comparable and accurate analytical data. No RMS' are available for regulated substances in typical electrotechnical polymers like ABS, PS, ABS/PC, etc. No RMS' are available for regulated substances in printed wiring boards.

### 15.1 Commercially Available Reference Materials (CRM)

There exist a variety of commercially available reference materials, mainly in polymeric and metallic matrices, but also, to a lesser degree, in glass and ceramic matrices. These materials have been specially formulated (doped) with the five elements of concern (Pb, Cd, Hg, Cr and Br), possibly with other elements present 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 20 gives an overview over existing CRMs suited for regulated substances in electrotechnical products.

**Table 20: CRMs suitable for regulated substances**

Substance	CRM	Comment
PBBs / PBDEs	Not available	BAM: Round robin test (final report expected at the end of 2004) ABS, PS with OctaBDE; PUR foam, epoxy resin with PentaBDE
Total Br	BCR-680, BCR-681	Plastics packaging and packaging material; certification of mass fractions of As, Br, Cd, Cl, Cr, Hg, Pb and S in polyethylene
Cr VI	BAM-S004	Glass for cosmetics; certification of mass fractions of hexavalent chromium and of total chromium in glass
Total Cr	BCR-680, BCR-681 BAM-S004	See above (Comment, Total Br) See above (Comment, Cr VI)
Hg	BCR-680, BCR-681	See above (Comment, Total Br)
Pb	BCR-680, BCR-681 BCR-126A	See above (Comment, Total Br) Certification of a lead glass
Cd	BCR-680, BCR-681 VDA-001 to VDA-004	See above (Comment, Total Br) Association of German Automobile Manufacturers; Certification for cadmium in polyethylene

### 15.2 In-House Reference Materials

Where commercially available materials do not exist, laboratory specific reference samples may be created. The process for creating these materials is the same as above, although the verification process will not be as complete, as multiple laboratories will not be conducting the analysis. The in-house reference material must be documented for all analyses conducted using the reference.

### 15.3 Creation of New Certified Reference Material

In the interest of uniformity, it is desirable to create certified reference materials for all matrices, including both the upper and lower concentration levels. The steps to creating a certified reference material are as follows:

- Determine the concentration levels for each of the elements of concern. Contract with a manufacturer of the desired matrix (polymer, metal, glass, ceramic, etc.) to prepare samples to the previously identified specifications.
- Provide samples of this material to multiple laboratories for analysis. Analytical methods that may be used include atomic absorption spectrometry; inductively coupled plasma spectrometry; inductively coupled plasma optical emission spectrometry; instrumental

neutron activation analysis; instrumental photon activation analysis; titration; and others as appropriate.

- c) The results of the inter-laboratory tests are to be analyzed and a variance determined. If the variance between laboratories is deemed acceptable, the average concentration level obtained will become the certified value for that element.



## **Annex A** (informative)

### **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 (resistors, 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 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. Moreover, exemptions exist for certain technical applications (e.g. the use of mercury in light bulbs and the use of lead in glass or ceramic materials). So, products may contain restricted 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.

A good example of the practical challenges of testing a finished product can be seen by examining the EU requirements. The EU has defined restricted substance thresholds at the “homogeneous material” level, making testing of a typical electronic product impossible from a practical standpoint. As noted previously, a typical electronic product (e.g. PC, cell phone, etc) may be made up of thousands, if not tens of thousands of homogeneous materials making complete testing of the product impractical due to cost, time and sample preparation constraints.

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 compliance using the test methods identified in this standard.

#### **A.2 Scope**

This Appendix will be limited to providing general guidance for a practical approach toward the testing of electronic products. 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 industry sectors that manufacture the products.

### 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 4 below illustrates the various levels of evaluation.

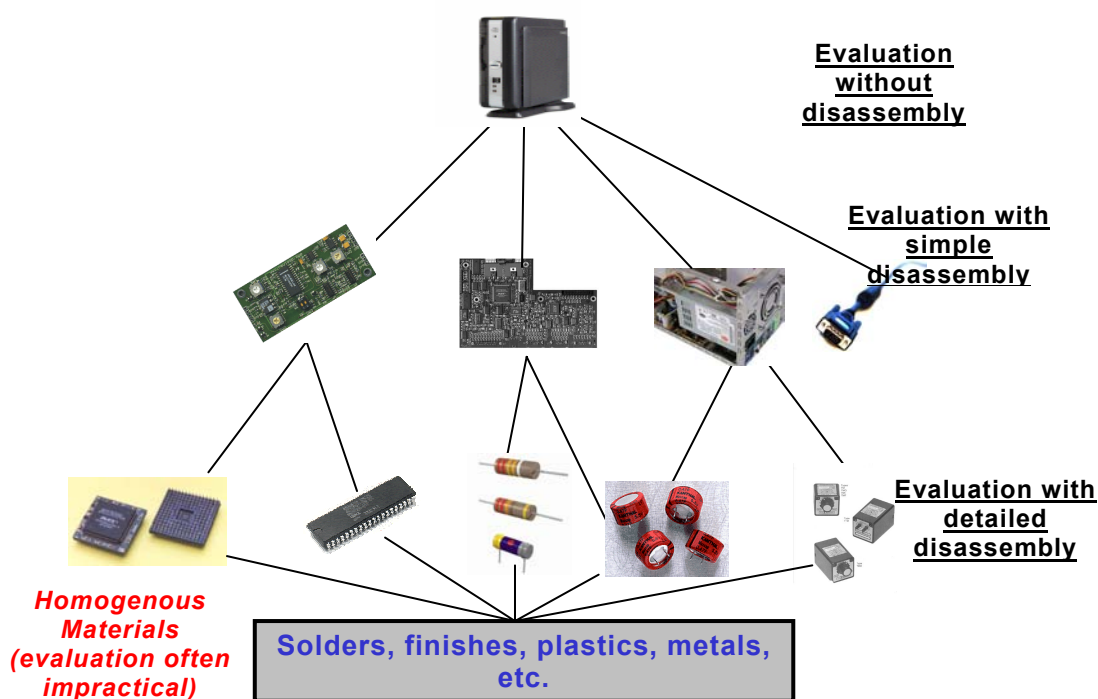


Figure 4: Evaluation Levels for Testing

#### 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 chapter 6 of this standard.

Table 21 lists the historical use of restricted substances in common 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 these applications.

Table 21: Historical Use of Restricted Substances in Common External Parts

External Part	Restricted Substance	Historical Use
Plastic enclosures, fasteners, clips, screws, etc.	Lead	Additive to plastic
	Cadmium	Additive to plastic; plastic colorant
	PBDEs	Flame retardant

Glass and ceramics	Lead <sup>1</sup>	Additive to glass
Metal enclosures, fasteners, clips, screws, etc	Hexavalent Chromium	Plating
Cables, cords, wires	Lead	Additive to plastic; stabilizer
	Cadmium	Additive to plastic; stabilizer
Decorative name plates, buttons, etc	Mercury	Additive to certain plastics; curing agent

<sup>1</sup>Lead in glass and ceramics is exempt under the EU RoHS Directive

Advantages of evaluation without disassembly are:

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

Disadvantages of evaluation without disassembly are:

- Cannot evaluate internal parts which may contain restricted 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 chapter 6 to 14 of this standard and illustrated in Figure 1 of this standard.

Table 22 lists the historical use of restricted substances in common 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.

Disadvantages of evaluation with simple disassembly are:

- May void product warranty
- May not allow assessment of all homogeneous materials

**Table 22: Historical Use of Restricted Substances in Common Internal Parts**

Internal Part	Restricted Substance	Historical Use
Plastic parts, housings, fasteners, clips, screws, etc.	Lead	Additive to plastic
	Cadmium	Additive to plastic; plastic colorant
	PBDEs	Flame retardant
Glass and ceramic parts such as resistors, diodes, etc.	Lead <sup>1</sup>	Additive to glass
Metal fasteners, clips, screws, etc	Hexavalent Chromium	Plating
Cables, cords, wires	Lead	Additive to plastic; stabilizer
	Cadmium	Additive to plastic; stabilizer
Printed circuit boards	Lead	Solder, finishes
Electrical components	Lead	Solder on terminal finishes
Inks	Lead	Additive
	Cadmium	Additive
	Hexavalent Chromium	Additive
Switches, relays	Mercury	Component of switch/relay
Bulbs	Mercury <sup>2</sup>	Used in florescent bulbs

<sup>1</sup>Lead in glass and ceramic parts is exempt under the EU RoHS Directive

<sup>2</sup>Mercury in florescent bulbs is exempt under the EU RoHS Directive

### 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 restricted substances (see Tables 21 and 22).

It should also be noted that when testing for certain restricted substances, detailed disassembly may not result in appreciably better results. For example, one of the most common uses of lead in electronics is the solder used to attach components to a printed circuit board. Although relatively small amounts of solder are used this application (3-5 grams per board), the lead content of the solder is significant enough (30-40% by weight) that its presence is very evident during product testing. As a result, it is not necessary to destructively disassemble the printed circuit board to test only the solder material. To illustrate this point, Table 23 contains the results of a recent study by the High Density Packaging User Group (HDPUG). The study evaluated the lead content of select printed circuit boards and integrated circuits using test methods similar to those described in Section 16 of this standard. If used, lead consistently showed up in concentrations far exceeding future legal thresholds. Therefore, further testing of homogeneous materials would add little value in this case, although in order to remedy the situation, additional investigation may be required to identify the homogeneous material or materials which represent the source of lead.

**Table 23: Lead Content of Select Printed Circuit Board Assemblies and Integrated Circuits (Source: HDPUG, Design for Environment Phase I Report, Feb 2003)**

Part	Average Lead Content	Future Regulatory Threshold <sup>1</sup>
Network interface card	10,000 ppm	1000 ppm
PC motherboard	28,000 ppm	1000 ppm
Telecommunications board	37,000 ppm	1000 ppm
Integrated circuit	10,000 ppm	1000 ppm

<sup>1</sup>EU RoHS sets regulatory limits on lead of 0.1% by weight of homogeneous material.

#### A.4 Additional Guidance

This section 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 24: Historical Use of Restricted Substances in Plastic Colorants**

Colorant	Restricted Substance
Brightly colored plastics: Yellow Orange Red Green	Cadmium, Lead and chromium VI (as lead chromate)

**Table 25: Historical Use of PBB/PBDE in Plastic Resins**

Plastic Resin	Compatible with PBB/PBDE?
Polystyrene (PS)	Yes
High-impact Polystyrene (HIPS)	Yes
Acrylonitrile/Butadiene/ Styrene (ABS)	Yes
Modified Polyphenylene Ether (PPE)	No

Polycarbonate (PC)	No
PC+ABS	No

## 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 must be interpreted carefully with regards to compliance with the applicable standards. This is due to the fact that although compliance standards such as RoHS apply to concentrations of restricted substances in homogeneous materials, 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 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 restricted substance using the selected test method. If detailed information is available regarding the application of the restricted 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 restricted substances. Three examples for this are given below:

- Result for theoretical composite sample A: No detections of restricted substances. Caution with interpretation: Although no restricted 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 restricted 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 PPM lead. Caution with interpretation: Although a numerical result for a detected restricted 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 PPM for lead is satisfied in this sample.
- Result for theoretical composite sample C: 1500 PPM lead. Caution with interpretation: Although a numerical result for a detected restricted 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.