Procedures for the Determination of Levels of Regulated Substances in Electrotechnical Products

IEC ACEA ad hoc Working Group

Mission of the ad hoc Working Group:
Develop a normative document that will define test procedures that will allow the electrotechnical industry to determine the concentration 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

Goal of the ad hoc Working Group:
Develop a normative document for electrotechnical industry to be used by labs globally for OEMs, suppliers, NGOs, governments, etc. The normative document will be submitted as proposal for an IEC standard.

Outline

1 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.

2 Scope

This normative 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 normative document will not determine:

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

3 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

4 Terms and Definitions

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

a) 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
b) 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
c) Homogenous Material: A homogenous material is made up of one or more substances that is of uniform composition throughout that cannot be mechanically disjointed into different materials.
d) Qualitative Screening: An analytical approach with the primary goal verifying the absence or presence of an element of interest (analyte) in tested material
e) Quantitative Screening: An analytical approach with the primary goal to quantify the concentration of an element of interest (analyte) in tested material
f) Polymer materials: Polyethylene, polyvinyl chloride, epoxy resin, polyamide, polycarbonate ABS resin, polystyrene, etc.
g) Metallic materials: Fe-alloys, Ni-alloys, Sn-alloys, Al-alloys, Mg-alloys, Cu-alloys, Zn-alloys, precious metals alloys
h) Electronics (PWBs/Components): Circuit boards, wiring materials, contacts, resistors, capacitors, cords, connectors, etc.
i) Analyte: Substance or element tested for
j) Matrix: The material or substance, form or state in which the analyte is embedded.

k)
l) Other terms and definitions are found in the terms and definition sections of the test procedures

5 Test Procedure Overview

5.1 Test Procedure Scope

The content of the test procedure described 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 (incl. opportunities & risks)
- References, normative references, reference methods and reference materials
- Terms and definitions
- Apparatus / Equipment and materials
- Reagents
- Sample preparation
- Test procedure
    - Calibration
    - Instrument performance
    - Sample analysis
    - Calculation of analytical results
    - Test report
    - Quality control

The first point includes the scope of the method, the best 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 will 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. ISO) are strongly encouraged.

5.2 Test Procedure Flow

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

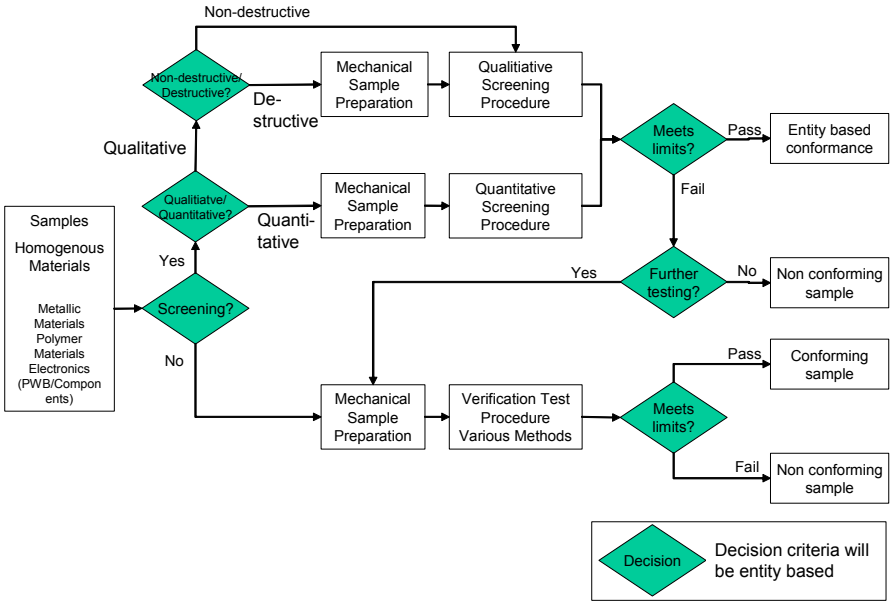

Figure 1: Flowchart of the Test Procedure

After obtaining the sample, 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 procedure to obtain the sample is not described in this normative document. This procedure is described in a separate guidance document in Annex N.

The screening test procedure can be carried out either qualitatively or quantitatively. The qualitative screening will indicate whether a substance is present or not, but may not give accurate information about the concentration of substance present. The quantitative screening procedure will provide results expressing the concentration of substance(s) present.

Qualitative screening can be carried out either by directly measuring the sample (non-destructive) or by going first through a mechanical sample preparation step (destructive). 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 may be necessary.

For the quantitative screening a mechanical sample preparation is mandatory. Mechanical sample preparation is the same for both the qualitative and the quantitative screening, as well as for the verification test procedure. It consists of cutting, grinding and homogenization of the sample.

Both the qualitative and the quantitative screening of a sample is performed using either an EDXRF (Energy Dispersive X-Ray Fluorescence) or a WDXRF (Wavelength Dispersive X-Ray Fluorescence) device. It must be noted that the screening test procedure should be performed under controlled conditions, as either EDXRF or WDXRF have limitations to its use and the applicability of the results obtained, although its fast and resource efficient way of analysis has its merits particularly for the demands of the electrotechnical industry.

After the screening test procedure it can be decided if the sample meets the limits based on the entity's criteria for regulated substances or if further testing is required.

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). 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.

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

5.3 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.

5.4 Qualitative and Quantitative Screening Test Procedure

Both the qualitative and the quantitative screening of a sample is performed using either an EDXRF (Energy Dispersive X-Ray Fluorescence) or a WDXRF (Wavelength Dispersive X-Ray Fluorescence) device, which x-rays the content of the sample. Both handheld and desktop types of equipment are suitable. It must be noted that the screening test procedure should be performed under controlled conditions, as the use of XRF has limitations to its use and the applicability of the results obtained, although its fast and resource efficient way of analysis has its merits particularly for the demands of the electrotechnical industry.

5.5 Verification Test Procedure

The verification test procedure of a sample is done using a variety of analytical methods tailored to the regulated substances and the material of the sample, which can be either plastics, metals or electronics in form of populated PWBs or components. The use of the verification test procedures will ensure results with less error, however taking 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)**
Sample preparation		Direct measurement, Grinding Microwave digestion Acid digestion Dry Ashing Solvent extraction	Direct measurement, Grinding, Acid digestion	Grinding Microwave digestion Acid digestion Solvent extraction
Analytical technique definition (incl. typical margins of errors)	PBB/PBDE	**See Table 2**		
	Cr VI			
	Hg			
	Pb/Cd			
References (material, methods) for comparison		BCR-680, BCR-681 In-house references	Commercial Solid Metal Standards	None commercially available, In-house references
Limitations & Information delivered				

Table 2: Details of the of the verification test procedure

	Substance	**Polymer Materials**	**Metal Materials**	**Electronics (PWBs/Components)**
Analytical technique definition (incl. typical	PBB/PBDE	**GC/MS** (including FT-IR)	NA	**GC/MS** (including FT-IR) HPLC/UV

margins of errors)		HPLC/UV		
	Cr VI	NA	**Spot test (ISO 3613) Alkaline Digestion & Colorimetric Method (EPA 3060A)**	NA
	Hg	**ICP-AES** ICP-MS CV AAS AFS		
	Pb/Cd	**ICP-AES** AAS ICP-MS		

Bold: Preferred Method
Normal: Acceptable Method

6 Procedure for Mechanical Sample Preparation

6.1 Scope, Application and Summary of Method

The purpose of this document is to provide practical guidance for the mechanical sample preparation step using the procedures described in the IEC ACEA ad hoc Working Group document.

This document is limited to providing general guidance for a practical approach toward the mechanical sample preparation of electrotechnical products. Due to the vast number and diverse nature of electronic products, it is not possible to cover all electrotechnical product sample in detail in this document. If detailed guidance is needed by product type or product family, such guidance should be developed by the individual industry sector TCs that manufacture the products.

In order to allow reproducible screening results the sample material should be as homogeneous as possible (in case of non-homogeneous materials) and show a consistent grain size distribution and density of the sample (for homogeneous materials).

6.2 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

6.3 Terms and Definitions

a) n.a.

6.4 Apparatus / Equipment and Materials

a) Cutting mill with 4 and 1 mm stainless steel bottom sieve (Retsch SM2000 or similar)
b) Centrifugal mill with 25µm tungsten carbide (WC) coated steel sieve, 6-fold WC coated rotor, (for homogenous plastic material a 1 mm steel sieve is appropriate) (Retsch ZM100 or similar)
   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) Vibratory Feeder (Retsch DR100 or similar)
d) Mixer (Turbula T2F or similar)
e) Analytical balance: Capable of accurate weighing to 0.0001 g

f) Brushes (different sizes)
g) Paper
h) Scissors, Heavy Plate Shears
i) 250 ml Glass Beaker
j) Liquid Nitrogen (N2)
k) Powder Funnel
l) Gloves
m) Safety glasses

6.5 Procedure

6.5.1 Sample

The sample to be analyzed should be a homogenous material, e.g. a polymer material, a metallic material or electronics. Guidance on how to get to this sample should be developed by the entity, the individual industry sector that manufactures the product or by TCs of the product group.

6.5.2 Cutting

Samples are precut to a size of no more than 2×10×10 cm^3.
Electronics: Samples are precut to a size of 4x4 cm using heavy plate shears
Polymer Materials: Samples are precut to a size of 5x5 mm using heavy plate shears or/and scissors. Thin polymer foils are to be cut into small pieces with a shear.

6.5.3 Coarse grinding

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**.**

6.5.4 Homogenizing

The resulting coarse powder is homogenized 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.

6.5.5 Fine grinding

Cool the 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.

7 Qualitative Screening by XRF Spectrometry

7.1 Scope

This document describes the procedure for the qualitative screening of regulated substances found in electrotechnical products using X-ray fluorescence (XRF). It covers parts and all material types such as polymers, metals and electronics.

Qualitative screening can be carried out either by directly measuring the sample (non-destructive) or by going through a mechanical sample preparation step (destructive). A screening of representative samples or uniform materials (such as plastics) can be done non-destructively, while for other samples (like a populated printed wiring board) mechanical sample preparation may be necessary.

The sample is irradiated by the beam emitted from an X-ray source. The resultant, characteristic X-rays of elements present in the sample tested are measured and converted to mass percent concentrations of elements.

Qualitative screening with X-ray fluorescence spectrometric analysis employs a qualitative analytic method to identify presence of regulated substances. Compared to other analytical procedures this test method offers high throughput, minimal or no sample preparation and wide dynamic range of measured concentrations. The equipment specified is in most cases less expensive than that required for alternative methods. Depending on the acceptance criteria in place for the controlled substances and performance of the analyzer used this test may or may not be conclusive. Should the latter be the case, this test must be followed either by quantitative screening analysis or by another verification test procedure that determine the presence and the concentration of controlled substance in the sample.

It must be noted that X-ray fluorescence spectrometric analysis only provides information on the presence of regulated substances in their elemental form. Special attention is needed e.g. for Chromium and Bromine, where the result will reflect the determination of presence of total Chromium and total Bromine, and not that for the regulated hexavalent chromium and PBB and PBDE. Therefore, 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. 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.

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.

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 agreement with local regulations. In addition, the personnel using the equipment should be properly trained in pertinent safety matters.

7.2 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 Wavelenght-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-VCH

e) ISO 20847:2004, Petroleum products – Determination of the sulfur content of automotive fuels – Energy-dispersive X-ray fluorescence spectrometry
f) ISO 8754:2003, Petroleum products – Determination of the sulfur content – Energy-dispersive X-ray fluorescence spectrometry
g) ISO 14596:1998, Petroleum products – Determination of the sulfur content – Wavelength-dispersive X-ray fluorescence spectrometry
h) van Grieken R. "Handbook of X-Ray Spectrometry" Marcel Dekker Inc.
i) VDA Reference Material No 001 through 004, Institute for Reference Materials and Measurements (IRMM), Geel, June 1993.
j) Certified Reference Materials BCR-680, and BCR-681, Trace Elements in Polyethylene, European Commission, Community Bureau of Reference – BCR, Brussels, January 2000.

7.3 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 is a direct measure of 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 realization of the XRF Spectrometry:
   - WDXRF spectrometry (Wavelength dispersive): Spectrometry in which X-rays emanated from sample are sorted according to their wavelengths rather than energy by dispersing element such as crystal or multilayer, and then only detected by (typically) gas-filled or scintillation detector.
   - EDXRF spectrometry (Energy dispersive): Spectrometry in which X-rays from sample are sorted according to their energy in a detector which plays a double role; of the dispersive device and of the detector itself at the same time.
b) Excitation X-rays: X-rays emitted by spectrometer's x-ray source and directed at a sample to induce X-ray fluorescence of the elements in a sample. Excitation X-rays can be generated by an X-ray tube or by an appropriate radioisotope source.
c) Secondary target method: For selective or more effective excitation of the element(s) in a sample X-rays emitted from a source are first directed at a target of appropriate pure metal, whose characteristic X-rays are then used to induce the X-ray fluorescence of sample elements. It is used mainly in the energy dispersive XRF spectrometers.
d) Primary beam filter: A thin foil (usually but not always made of pure metal) placed in the beam of excitation X-rays, between the excitation source and specimen, to change the spectral distribution of the excitation X-rays. Typically, this filter would have thickness selected in such a way that it would be opaque for lower energy X-rays and transparent for higher energy X-rays emitted by the source.
e) Synthetic multilayer film: Two or more layers of materials stratified for use as X-ray dispersive element.
f) Detector of X-ray radiation: Device used to detect the X-ray photon and convert its energy into electric pulse of amplitude proportional to energy of the photon. Examples are proportional counter (gas flow type and sealed type) and scintillation counter for wavelength dispersive X-ray fluorescence spectrometer (WDXRF). For energy dispersive X-ray fluorescence spectrometer (EDXRF) usually solid state, semiconductor detectors are used such as Si(Li) or silicon p-i-n diode.
g) Energy Resolution of Detector: A critical parameter of detector of radiation that reflects its ability to separate X-rays of adjacent energies. For detectors used in XRF Spectrometry this parameter is expressed as the Full Width at Half Maximum (FWHM) of the peak of the manganese K-alpha line irradiated directly at the detector at total count rate in spectrum not exceeding 1000 counts per second. For solid state detectors the FWHM is expressed in units of energy, electron-Volts, while for gas-filled proportional detectors it is expressed in percent as a ratio of FWHM to energy of the Mn K-alpha peak.

h) Calibration samples: Set of samples with very well known compositions used to develop or update the calibration curve(s) for the element(s) of interest.
i) Standardization sample: A sample used to confirm proper operation of the instrument. This sample is measured always under the same conditions and the results of its analysis including analytical errors must be within an a priori specified acceptance range in order for the instrument to be used for quantitative analysis of an unknown material. This sample must not change its composition over time, and its composition should be as similar to the unknown material tested as practically possible. This sample is often referred to as "Check Sample" or "Reference Sample".
j) Analytical Background: The intensity of radiation measured from spectrum of a sample in the region specific to the element of interest (analyte) when this element is not present in sample. Modern XRF Spectrometers automatically account for the background.
k) Escape peak: This is a companion peak observed on X-ray spectrum at an energy lower than the energy of the parent, characteristic X-ray peak by energy of the characteristic X-rays of the detector material. For silicon detectors escape peak occurs at 1.74 keV left off the parent peak, while for argon gas-filled detector it will show at 2.96 keV left off the parent peak. Typical intensity of this peak is about 1% of the parent peak. The smaller the detector the more likely the occurrence of escape peak. Modern XRF Spectrometers automatically eliminate escape peaks from the spectra.
l) Sum peak: An artificial peak on X-ray spectrum occurring at an energy which is a multiple (usually the double) of an energy of a characteristic X-ray peak. This phenomenon is the result of the spectrometer inability to distinguish two consecutive photons when they occur within a very short time (typically within few hundred nanoseconds). This phenomenon is observed at higher count rates that challenge resolution time of the spectrometer. Modern XRF Spectrometers automatically correct for this spectral artifact.
m) Statistical error of counting: Fluctuation in counts (or count rate) observed during repeated measurements of X-ray intensity of the element in sample, which is due solely to the random nature of interaction of X-rays with matter. This fluctuation has Poisson distribution and therefore, its measure can be expressed as the square root of counts.

7.4 Apparatus/Equipment and Materials

a) X-ray fluorescence spectrometer (XRF): Any X-Ray Fluorescence Analyzer (Spectrometer) may be used if its design incorporates, as a minimum, the following features:
    - Source of excitation X-rays. X-ray source capable of generating x-rays of energies up to and above 35 keV. An X-ray tube or radioisotope is commonly used as source of X-ray excitation.

Warning: If a radioactive source is used, it must be well shielded to international standard requirements and, therefore, not present any safety hazard. Attention to the source is only to be carried out by a fully trained, competent and authorized person using the correct shielding techniques. Operation of analyzers using X-ray tube sources must be conducted in accordance with the manufacturer's safety instructions and local regulations.

    - Means of sample presentation for analysis. An analyzer must have the provision to present sample for analysis in a consistent and repeatable manner. This may be a sample holding mechanism, a sample table or a sample cup holder (in case when liquid or powdered material is amnalyzed) - as is typical in a laboratory type instruments, or a specially configured flat, external surface with the window that is pressed directly against the measured sample- a feature typical for the hand-held portable instruments.
    - X-ray detector. A detector of X-rays with sufficient sensitivity within the energy range from 2 to 35 keV, with energy resolution not worse than 220 eV. Solid state detectors such as liquid nitrogen cooled Si(Li) detectors or "room temperature" thermoelectrically cooled p-i-n silicon diodes are suitable for the task of X-ray detection and counting.
    - Filters or other means of modifying or optimizing the primary X-ray radiation in order to improve analytical performance of the instrument.

- Signal conditioning and data handling electronics and software that include the functions of X-ray intensity counting, spectrum processing and alghoritms to convert the measured intensities (count rates) of elements into their mass concentration of sample..
- Display, printer or other means of communication with the operator to report the results of analysis and accept operator's feedback.

There are two types of X-ray fluorescence spectrometers - wavelength dispersive X-ray fluorescence spectrometer (WDXRF) and energy dispersive X-ray fluorescence spectrometer (EDXRF). Both can be used for qualitative screening. Independent from the X-ray fluorescence spectrometer which is used, the equipment needs to be able to distinguish between materials that contain regulated substances below or above the limits given in Table 3.

Table 3: Qualitative screening detection limits in mg/kg (ppm) for regulated substances in various matrices

Substance	Polymer Materials	Metallic Materials	Electronics
Cd	50	100	100
Pb	100	200	200
Hg	100	200	200
Br	50		100
Cr	100	200	200

As these limits are to be seen as limits of quantification, the analyzer should be capable of achieving detection limits (LOD) at a level of a third of the screening limits. This requirement is listed in table 4, where the detection limit is calculated following the IUPAC definition of:

$$\mathrm{LOD} = \frac{3 \cdot \sqrt{\mathrm{U}} \cdot \mathrm{C}_0}{\mathrm{N}_0}$$ where:

U: Background intensity (counts)
C_0: Concentration of sample (close to LOD) (ug/g)
N_0: Net pulse intensity (counts)

Table 4: Desired detection limits in mg /kg (ppm) to fulfill the qualitative screening detection limits for different substances in various matrices

Element	Polymer Material	Metallic Material	*Electronics*
Cd	15	30	*30*
Pb	30	60	*60*
Hg	30	60	*60*
Br	15		*30*
Cr	30	60	*30*

Note: These detection limits should be determined based on measurements of appropriate Certified Reference Materials (CRMs), for example such as BCR-680 and BCR 681 or equivalent if available. Otherwise, well characterized samples might be used.

7.4.1 Reference samples

Commercially Available
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.

In XRF analysis, the semi-quantitative programming of the instrument can be modified, or corrected, using the reference material(s). The software used by the instrument determines the concentration of each element in each material(s). The concentrations are then corrected (i.e., the known values from the certified reference material replace the values obtained by the instrument), creating a standard reference material. This material can then be used in the analysis of unknown materials.

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.

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:

a) 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.
b) 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.

7.5 Test Procedure

7.5.1 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.

7.5.2 Calibration

a) If the instrument calibration is not required, proceed to 7.5.3. This is often the case with instruments which use so called fundamental parameter method approach.
b) If the instrument requires calibration, it should be performed by following the guidelines in the instrument's users manual. There are two typical approaches to instrument calibration: empirical and fundamental parameters based.
    - Empirical calibration involves measurement of set of calibration samples. Samples used for calibration should resemble in composition as close as possible the unknown material. Concentrations of analytes in calibration samples should be well known and should bracket the expected concentrations in the unknown material, and should not be obtained by dilution. Since typically at least 5 samples of different concentration is required per analyte to calibrate the instrument as many as 25 or more samples may be required. After samples are measured, the X-ray intensities of each analyte are correlated via multiple linear regression equation with concentration data for the analyte.
    - In fundamental parameter calibration approach one may need only one calibration sample per sample matrix type. If the fundamental parameter calibration is to be performed by the user at all, the details of such procedure will be given in users manual.
    - Regardless of the type of calibration employed in the instrument, its performance must be verified after each calibration or calibration update as per Section 7.5.3.

7.5.3 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. 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 the apparatus may be used for analysis of the unknown material. Some manufacturers may provide with 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.

7.5.4 Presentation of Sample for Measurement

a) If a section including the specimen to be measured can be placed inside the specimen chamber of the desk top X-ray fluorescence spectrometer in such a way that the specimen itself 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. 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. As a general rule all samples must completely cover the measuring window of the spectrometer, and 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. However, due to individual variations by 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.
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 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.

7.5.5 Measurement

a) To analyze the specimen follow the instructions provided in the operating manual of the instrument which, as minimum, should include the following basic steps:
    - Place the sample in the measurement position (chamber) and perform measurement in compliance with instructions in users' manual. In case of portable instrument, place the measuring window of the analyzer against the surface of the sample and perform measurement by initiating the spectrum acquisition of a sample for a predetermined measurement time.
    - At the conclusion of the measurement the instrument should typically provide the measured concentration(s) of analyte(s), or a numerical value related to the concentrations of the elements in sample.
    - If the instrument does not store the results automatically, record the results and any pertinent information. Continue with measurements.
    - Every few unknown samples perform measurement of the reference sample as in Section 7.5.3. It is recommended that either the SOP supplied by manufacturer is followed or the user's own SOP (if such exists) is followed as to how often the reference sample must be measured to maintain integrity of the results.
b) 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 (such as type of isotope or X-ray tube High Voltage, current and primary beam filter, as well as measurement time per sample). These conditions are instrument specific and typically, this information is found in analyzer's instruction manual. As a general guidance the user of this method is advised that spectral interferences existing between elements and matrix composition

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. Following, table 5 shows characteristic X-ray lines intensities, which are recommended for individual analytes:

Table 5: Characteristic X-ray lines intensities for individual analytes.

Analyte	Primary Line	Secondary Line
Cadmium, Cd	Kα	
Lead, Pb	Lα	Lβ
Mercury, Hg	Lα	
Chromium, Cr	Kα	
Bromine, Br	Kα	Kβ

c) Measurement time per sample necessary for detecting controlled substance varies with instruments and matrix and has to be chosen to fulfill the criteria from 7.4. Typical measurement times may vary from 30 to 300 sec per sample, depending on analyte, sample type and instrument model.

7.5.6 Test 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
b) Unique identification of report (such as serial number) and of each page and total number of pages of the report
c) Description and identification of the sample
d) Date of receipt of sample and date(s) of performance of test
e) A reference to this IEC standard
f) Which processes, procedures and apparatus were used
g) Any details not specified in this standard which are optional, and any other factors which may have affected the results.

Corrections or additions to a test report after issue shall be made only y 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.

7.6 Method Evaluation

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

7.7 Annex (Informative)

7.7.1 Interpretation of results according to RoHS

a) If the qualitative analysis gives a result for all elements, which is lower than the lower limit than listed in table 3, the sample is tested ok according to RoHS.
b) If the qualitative analysis gives a result for any element, which is higher than the higher limit than listed in table 3, the sample is tested not ok according to RoHS.

7.7.2 Matrix 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 subsequent emission of 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.

7.7.3 Sample Size and Thickness Considerations

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. As a general rule all samples must completely cover the measuring window of the spectrometer, and 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. However, due to individual variations by 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.

8 Quantitative Screening by XRF Spectrometry

8.1 Scope

This document describes the procedure for quantitative screening of regulated substances found in electrotechnical products. It covers parts and all material types such as polymers, metals and electronics.

The sample to be analyzed is prepared by adequate means of mechanical sample preparation. A representative specimen is taken and irradiated with X-ray for measurement of X-ray fluorescence intensity for quantitative screening of regulated substances. Quantitative screening with X-ray fluorescence spectrometric analysis employs an analytical method based on reference materials with comparable composition.

It must be noted that X-ray fluorescence spectrometric analysis only provides information on the presence of regulated substances in their elemental form. Special attention is needed e.g. for Chromium and Bromine, where the result will reflect the determination of presence of total Chromium and total Bromine, and not that for the regulated hexavalent chromium and PBB and PBDE. Therefore, 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. 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.

The analytical method must be calibrated carefully 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) Cd :Interferences possible from Br, Pb, Sn, and Sb
b) Pb: Interferences possible from Br
c) Hg: Interferences possible from Br, Pb and in case that the samples contain Ca and Fe in high concentrations
d) Cr: Interferences possible from Cl
e) Br: Interferences possible from Fe and Pb

In addition to that the thickness of the sample has impact on the fluorescence intensity as well (especially on the determination of Cd. The reference samples should have a thickness comparable to that of the specimen.

XRF in general is a comparative analytical method. The analytical results achieved are always based on the analytical calibration. Accepted reference methods are described in this document in chapters 10 to 16.

8.2 Normative references

The following referenced documents are 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) C 982 Guide for Selecting Components for Energy-Dispersive X-Ray Fluorescence Systems
b) C1118-89(2000) Standard Guide for Selecting Components for Wavelenght-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-VCH
e) van Grieken R. “Handbook of X-Ray Spectrometry” Marcel Dekker Inc.
f) Certified reference materials BCR-680 and BCR-681
g) Certified reference materials VDA 1-4

8.3 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 is a direct measure of 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 realization of the XRF Spectrometry:
    - WDXRF spectrometry (Wavelength dispersive): Spectrometry in which X-rays emanated from sample are sorted according to their wavelengths rather than energy by dispersing element such as crystal or multilayer, and then only detected by (typically) gas-filled or scintillation detector.
    - EDXRF spectrometry (Energy dispersive): Spectrometry in which X-rays from sample are sorted according to their energy in a detector which plays a double role; of the dispersive device and of the detector itself at the same time.
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 X-ray fluorescence intensity into corresponding pulse. Examples are proportional counter (gas flow type and sealed type) and scintillation counter for wavelength dispersive X-ray fluorescence spectrometer (WDXRF). For energy dispersive X-ray fluorescence spectrometer (EDXRF), semiconductor detector with high-energy resolution (better than 220 eV referred to Mn Kα to resolve radiation from Hg and Pb) is recommended. The semiconductor detector can be cooled with liquid nitrogen or cooling element, if necessary.

8.4 Apparatus/Equipment and Materials

a) X-ray fluorescence spectrometer (XRF): Consists of X-ray excitation source, means of sample presentation, X-ray detector, data processor and control system. There are two types of X-ray fluorescence spectrometers -- wavelength dispersive X-ray fluorescence spectrometer (WDXRF) and energy dispersive X-ray fluorescence spectrometer (EDXRF).

Warning: Operation of analyzers generating or using X-ray radiation during operation, such as X-ray tube or radioisotope sources must be conducted in accordance with the manufacturer's safety instructions and local regulations. If a radioactive source is used, it must be well shielded to international standard requirements and, therefore, not present any safety hazard. Attention to the source is only to be carried out by a fully trained, competent and authorized person using the correct shielding techniques.

b) The analytical method should allow to distinguish between samples, which safely contain concentrations, which are below the tolerated values and those, which are clearly higher than the tolerable values. In case, that this statement cannot be committed clearly, additional investigation with other analytical methods are necessary.
c) Independent from the technique which is used, the following limits must be observed, where X marks the region, where further investigation is necessary. (The definition has to be confirmed by an inter laboratory study).

Table 6: Screening limits in mg/kg for different elements in various matrices

Element	Polymer Materials	Metallic Materials	*Electronics*
Cd	50< X <150	50< X <150	DL< X <250
Pb	700< X <1300	700< X <1300	*500< X <1500*
Hg	700< X <1300	700< X <1300	*500< X <1500*
Br	300< X		*250< X*
Cr	700< X <1300	700< X <1300	*500< X <1500*

The analyzer should be tested with substances with known composition in order to proof the performance. It is recommended to use minimum two test substances, where one should have concentrations of about 50 % of the lower limits and the second should have about 150 % of the upper limit.

The analyzer should be capable of achieving detection limits (LOD) listed in table 7, where the detection limit is calculated following the IUPAC definition of:

$$LOD = \frac{3 \cdot \sqrt{U} \cdot C_0}{N_0}$$

where
U: Background intensity (counts)
C0: Concentration of sample (close to LOD) (ug/g)
N0: Net pulse intensity (counts)

Table 7: Desired detection limits in mg /kg to fulfill the screening limits for different elements in various matrices

Element	Polymer	Metals	*Electronics*
Cd	15	30	*30*
Pb	30	60	*60*
Hg	30	60	*60*
Br	15		*30*
Cr	30	60	*30*

Note: These detection limits should be determined based on measurements of appropriate Certified Reference Materials (CRMs), for example such as BCR-680 and BCR 681 or equivalent if available. Otherwise, well characterized samples might be used.

8.4.1 Reference samples

Commercially Available
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.

In XRF analysis, the semi-quantitative programming of the instrument can be modified, or corrected, using the reference material(s). The software used by the instrument determines the concentration of each element in each material(s). The concentrations are then corrected (i.e., the known values from the certified reference material replace the values obtained by the instrument), creating a standard reference material. This material can then be used in the analysis of unknown materials.

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.

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:

a) 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.
b) 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.

8.5 Test Procedure

8.5.1 Spectrometer adjustment

Energize the apparatus according to the operation manual of the manufacturer. Due to the need for optical or electrical stability, the length of time required for temperature to stabilize varies by model.
To assure measurement stability, stability of the detector should be achieved, as specified by the manufacturer's guidelines.

8.5.2 Calibration

a) Follow the guidelines in the instrument's users manual when selecting the calibration samples using reference samples as defined in 7). The element concentrations must vary independently in the 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 reduced by:
    - calibration with fundamental parameters method (standardless)
    - calibration with fundamental parameters method (with a similar standard)
    - analysis using fundamental parameters plus empirical calibrations
b) Measurement requirements for quantitative screening test
    - Cadmium measurement employs the Cd-K series.
    - Lead measurement employs the Pb-L series.
    - Mercury measurement employs the Hg-L series.
    - Chromium measurement employs the Cr-K series.
    - Bromine measurement employs the Br-K series
c) Measure the calibration samples according to the instrument user's manual.
    - If the specimen is in liquid, powder or form or is a microscopic component, the sample cup can be washed thoroughly with appropriate quantity of alcohol or detergent and dried before use. Disposable window film should not be reused. To handle the window film, attention must be paid to handle the film on both ends and to avoid touching the measurement surface at the center.
    - The standard measurement time necessary for the quantitative screening varies with instrument and matrix and has to be adapted to fulfill the criteria from 7 c)
d) Perform the calibration according to the instrument user's manual.
e) Process quality control samples with concentrations as described in 7 c).
f) Repeated measurements of the quality control samples serves as instrument performance monitoring, when done regularly.

8.5.3 Quantitative screening test

a) Place the specimen in the measurement position in compliance with the method specified for each apparatus.
b) Perform measurement for a specified period of time, and measure X-ray intensity either in the X-ray fluorescence spectrum or the designated energy level.
c) Perform quantitative analysis.
d) Display and record analytic findings.

A possible interpretation of results is described in the annex (Chapter 8.6).

8.5.4 Test 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:

Name, address and location of any laboratory involved in the analysis

a) Unique identification of report (such as serial number) and of each page and total number of pages of the report
b) Description and identification of the sample

c) Date of receipt of sample and date(s) of performance of test
d) A reference to this IEC standard
e) Which processes, procedures and apparatus were used
f) Any details not specified in this standard which are optional, and any other factors which may have affected the results.

Corrections or additions to a test report after issue shall be made only y 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.

8.6 Annex (Informative)

8.6.1 Interpretation of results according to RoHS

c) If the qualitative analysis gives a result for all elements, which is lower than the lower limit than listed in table 1, the sample is tested ok according to RoHS.
d) If the qualitative analysis gives a result for any element, which is higher than the higher limit than listed in table 1, the sample is tested not ok according to RoHS.
e) If the qualitative analysis gives a result for any element, which is in the region defined intermediate, additional investigation needs to be performed.

8.6.2 Matrix 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 subsequent emission of 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.

8.6.3 Sample Size and Thickness Considerations

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. As a general rule all samples must completely cover the

measuring window of the spectrometer, and 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. However, due to individual variations by 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.

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

9.1 Scope, Application and Summary of Method

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. The samples are analyzed by gas chromatography/mass spectrometry (GC/MS) with the proper sample preparation and clean-up procedures. 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.

Greatest risks are the following:

a) The recovery of analyte can not be determined exactly with the polymers which are not dissolved in most of solvents.
b) According to the EU RoHS, the application of this method can be limited.
    - 1000 ppm as total PBDEs (sum of selected isomers): partly useful
    - 1000 ppm as each PBDE isomer or congeners: No Use
    - 100 ppm as total PBDEs: Very useful
    - 100 ppm as each PBDE isomer or congeners: Partly useful
c) Do not boil the samples with the solvents to dissolve without very careful safety direction(s) and guide lines

9.2 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 ($^{13}C_{12}$ mass labeled BDE mixture) from Wellington laboratory
    - BDE-CVS-E (1-5: Calibration solution) from Wellington laboratory
    - MBDE-139-IS ($^{13}C_{12}$ mass labeled hexa bromo diphenyl ether) from Wellington laboratory
    - Phenanthrene D_{10}
    - Materials from BAM
    - ABS, PS, PUR, Epoxyresin containing octa and penta BDEs
    - Materials synthesized in house
    - ABS-SAN, PC, PMMA containing deca BDE from Albemarle
    - ABS-SAN, PC, PMMA containing technical BDEs from unknown source

9.3 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) Calibration compound: 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) PFK: Perflurokerosene : the mixture of compounds used to calibrate the exact m/z scale in the MS
e) PFTBA: Perfluorotributylamine : the mixture of compounds to calibrate the exact m/z scale in the MS
f) Soluble polymer: Polymers which can be dissolved with the solvent(s) under the room temperature
g) Partly soluble polymers: Polymers which are swelled in the solvents or part of the polymer is dissolved with solvents under the room temperature
h) Non soluble polymer: Polymers which can not be dissolved with the solvents under the room temperature

9.4 Apparatus / Equipment and Materials

9.4.1 Apparatus

a) Laboratory fume hood
b) Balances capable of weighting 10 mg
c) Glass disposable pipets of 150 mm long x 5 mm ID
d) Soxhlet apparatus with condenser (50~100 ml of soxhlet extractor with 100 ml or more round flask)
e) Heating mental 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 (125-1000 ml), buchner funnel (15 cm), Beaker (100-500 ml), vials (1-2 ml), washing bottles

9.4.2 Equipment

a) Gas chromatography – temperature programmable with splitless injection port for capillary column
   - Column : (5%-phenyl)-methyl polysiloxane and temperature limit of 340 or more (length 15 m; inner diameter 0,25 mm; 0,1 µm film thickness (Recommendation : DB-5 HT or equivalent)
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. Shall capable of scanning from 200 or 730 amu (recommendation: 960) and produce a mass spectrum for PFK or PFTBA (recommendation: High PFK and Super high PFK)
   Warning: Usage of super high PFK can cause some damage to MS because of high viscosity!

9.5 Reagents

a) Sulfuric acid: Reagent grade or CMOS grade
b) Purified nitrogen gas
c) Solvents: GC grade or higher (Recommendation : Pesticide grade)
d) Mainly used: Acetone, tetrahydrofuran, toluene, hexane, methylene chloride, chloroform, methanol. Should be free of interferences.
e) Quartz or glass wool: Rinsed with methylene chloride or baked at 400 ℃ for 4 hours minimum
f) Silica gel:
   - Activated: 70-~230 mesh, rinsed with methylene chloride, activated at 130 □ 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 1.76 g of concentrated sulphuric acid
   - Basic silica gel: not recommended
g) Water: Hexane cleaned water
h) Calibration solutions

a) Labelled $^{13}C_{12}$ BDEs or 4,4'-dibromoonctafluro biphenyl (f) or Penathrene D10 as recovery standard for the analysis of PBDEs. Labelled ^{13}C12 PBB or 4,4'-dibromoonctafluro biphenyl (f) or Penathrene D10 as recovery standard for the analysis of PBBs

9.6 Sample Preparation

9.6.1 Sample Identification

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

9.6.2 Extraction

The samples are grinded to a size of 1.0 mm by the combination of cutting and mills under cooling with liquid nitrogen. Dissolve the samples (1.0g each) with 10 ml of the selected solvents determined in section 6.1 after addition of $^{13}C_{12}$-labeled PBDE(s) or the proper chemicals as recovery standard. Stir it for 1 hour with glass sealed magnet bar.

For the soluble and partly soluble polymers
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 and gel-purification. The liquid-liquid extraction should be done when the solvents are polar one. 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.

For the non soluble polymers
Without precipitation and liquid-liquid extraction, the polymers should be extracted by soxhlet for 16 hrs or more. For this case, toluene or tetrahydofuran 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 H_2SO_4 until colorless and then with hexane-rinsed water to make them neutral.

9.6.3 Sample cleanup and purification

Stop the one end of a glass column (20 mm X 350 mm) with 250 ml of reservoir with solvents rinsed glass wool. Add in sequence, 1 g of dehydrated sodium sulfate, 1 g of slica gel, 4g of acid modified silica gel, and 1 g of dehydrated sodium sulfate. Rinse the column with 30 ml of hexane and discard.
Add the sample concentrated at the previous steps. Elute the column with additional 130 ml of hexane and retain the entire elute. Evaporate this solution to a volume of about 1~2 ml and transfer to a glass bottle (6 mm x 13 mm).

9.7 Test Procedure

9.7.1 Calibration

a) Prepare in nonane or purchase as solutions or mixtures.
b) The commercially available calibration standard mixtures (Cambridge isotope laboratory or Wellington Laboratories) are recommended
c) At least, five different calibration solutions should be prepared within the range of linearity of the GC/MS
d) For the samples containing higher concentration of target isomers, the preparation of calibration solutions from the materials is recommended

9.7.2 Instrument performance

9.7.3 Sample Analysis

Inject 1.0 µl of the concentrated samples containing the internal 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 (5 min), 40 °C/min up to 200 °C (4.5 min), 10 °C/min to 325 (15 min). The injector temperature is held at 250 °C. Mass spectrometry (GC/MS) analyses are performed on the following conditions.

a) Resolution (1,000 m/e or more)
b) Ionization mode : Electron impact
c) Source temperature : 250 °C
d) Monitoring mode: Selected ion monitoring. Exact masses of the ions monitored are presented in Table 1. For the $^{13}C_{12}$ labeled internal standard, M+12 are selected.

1st analysis
Analysis the concentration of the sample obtained from 6-2. Calculate the concentration of the sample using the following equations (1&3). If the concentration is over the threshold value, the further process is not necessary. If not, 2nd analysis should be done.
* The operator should know the detection limit of the instruments

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

9.7.4 Calculation of Analytical Results

Prepare the calibration curve for each compound to be determined.

a) Equation 1 : the measurement of Calibration 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 = Rsm/Rst
- 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 (ppm) = [(Ys-B)/A]*R*Wcf
- C(ppm) = Unknown content of sample.
- Ys= area of the isomer of the sample
- Wcf = conversion factor (must including w/v ◊ w/w)

9.7.5 Test Report

a) Information on the analysts and sample (s)
- Material information
- The extraction solvents and amount
- Standard compounds (Type, Amount and Preparation)
- Operation condition of GC/MS with calibration compounds.
- Linearity and recovery rate of each isomer monitored.
- Results from blank test.
- Results (Total amount, Amount of each isomers)

b) Results from all quality assurance and quality control (QA/QC) tests

9.7.6 Quality Control

Refer to the sections from 9.1.3 to 9.8 of US EPA 1613.

9.8 Evaluation of the Method

This method is being evaluated by sixteen Korean analytical institutions with the reference materials prepared by Samsung Advanced Institute of Technology, Cheil Textile Company and Samsung Electronics.

9.9 Annex

Table 9: Reference masses for the quantification of PBDEs

	IONS Monitored in the extract		
Mono-BDEs	**247.98**	249.98	
Di-BDEs	325.89	**327.89**	329.89
Tri-BDEs	403.80	**405.80**	407.80
Tetra-BDEs	323.87	**325.87**	483.71
Penta-PDEs	401.78	**403.78**	561.62
Hexa-BDEs	481.69	**483.69**	643.52
Hepta-BDEs	559.60	**561.60**	721.44
Octa-BDEs	639.51	**641.51**	643.51(801.34)
Nona-BDEs	717.42	**719.42**	721.42(879.25)
Deca-BDEs	797.33	**799.33**	959.16

Optional ions for deca-PBDE : 231.8, 398.6, 400.5, 799.3
( ): Optional ions
Bold: Quantification ions
Under line: Identification ions.
For PBBs : PBDEs-16 (ex: Mono BB = 247.98-16=231.98)

10 Determination of PBB and PBDE in Polymer Materials by HPLC/UV

10.1 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

10.2 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

10.3 Terms and Definitions

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

a) Homogeneous Material: A material of uniform composition throughout that cannot be mechanically disjointed into different materials.
b) Applied material: A unit which cannot become further mechanically disjointed in single materials, such as multilayer materials and electronic components less than 1 g.

10.4 Apparatus / Equipment and Materials

10.4.1 Apparatus / Equipment

a) Extraction Unit: Behr SMA 12 heating block
b) HPLC system with low pressure gradient pump, autosampler, column oven and UV scanning detector, (e.g. P580 pump, ASI 100 Automated Sample Injector, STH 585 column oven and PDA 100 Photodiode Array Detector from DIONEX, Germany)
c) Further typical laboratory tools and equipment is necessary
d) The instrumentation can be replaced by items with similar functionality

10.4.2 Materials

a) Volumetric flasks
b) Adjustable Pipettes
c) 12x32 mm vials
d) Filter discs
e) Stationary phase: modified C18 column, (for example Macherey-Nagel Nucleosil CC 125/4 100-5 C18 "Nautilus" with pre-column CC 8/4 Nucleosil 100-5 C18 "Nautilus" (Macherey Nagel))

10.5 Reagents

a) Methanol (HPLC grade)
b) Water (HPLC grade)
c) KH_2PO_4 p.A.
d) $NaHPO_4$ 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)

10.5.1 Standard preparation / Stock solution preparation

a) Mobile Phase: 97% Methanol and 3% of buffered water. A phosphate buffer is used. The water was buffered by dissolving 0.1509 g KH2PO4 and 0.2477 g NaHPO4 in 100 ml of water. The run time is 12 min at a flow rate of 1 ml/min.
b) As sample solvent for the dissolution of pure standards and for the extraction of samples n-Propanol was used.

10.6 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. 100 mg of the sample is extracted in a soxhlet extractor for three hours using 70 ml of n-Propanol. After cooling to room temperature the extracts are filtered and filled up to a volume of 100 ml. 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.

10.7 Test Procedure

10.7.1 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.

10.7.2 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.

10.7.3 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 3 mL of sample and attach a syringe filter to the syringe. Discard 0.5 mL 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.

10.7.4 Calculation of Analytical Results

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

10.7.5 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.

10.7.6 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.

The documentation of quality for this method shall include:

a) Retention time reproducibility
b) Peak Area reproducibility
c) Calibration function
d) Linear Range
e) 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.

10.8 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 10. 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 10: 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 11 shows some exemplary results for the peak area reproducibility. Other wavelengths can be extracted form the three-dimensional chromatogram at any time. The three dimensional chromatograms are recorded using 2 nm resolution. Each of the wavelengths can be extracted from the data field.

Table 11: Peak Area Reproducibility Data

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

11 Screening for Hexavalent Chromium in Colorless and Colored Chromate Coating by Spot Test

11.1 Scope, Application and Summary of Method

This method provides procedures for the determination of hexavalent chromium in colorless and colored chromate coating. This method is adopted from ISO 3613: 2000(E), “Chromate Conversion Coatings on Zinc, Cadmium, Aluminum-Zinc Alloys and Zinc-Aluminum alloys---Test Methods”.

11.2 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) Certified reference material BCR-680 and BCR-681 (Cr in polyethylene)
c) Certified reference material BAM-S004 (glass containing hexavalent chromium)

11.3 Terms and Definitions

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

a) N/A

11.4 Apparatus / Equipment and Materials

a) N/A

11.5 Reagents

a) 1,5-diphenylcarbazide
b) Acetone
c) Ethanol (96%)
d) Orthophosphoric acid solution (75%)
e) DI water

11.6 Sample Preparation

Prior to the test, the sample surface shall be free of all contaminations, 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, or a suitable solvent at room temperature (not exceeding 35ºC). The samples shall not be subject to forced drying at temperature in excess of 35ºC. 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 papers 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 could be applied if they are proved to be more effective.

11.7 Test Procedure

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

Place 1 to 5 drops of test solution (prepared in procedure 1) on the sample surface. If hexavalent chromium is present, a red to violet color will appear within a few minutes. Ignore any color that appears much later, for example on drying.

For 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.

If the test shows positive for the sample, i.e. hexavalent chromium is present. A quantitative analysis shall be followed according to “Determination of hexavalent chromium by colorimetric method”.

11.8 Evaluation of the Method

N/A

12 Determination of Hexavalent Chromium by Colorimetric Method

12.1 Scope, Application and Summary of Method

This method describes the procedures to measure hexavalent chromium, i.e. Cr(VI), quantitatively in samples of metallic materials, polymeric materials, and electronics. 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 0.28M Na2CO3/0.5M NaOH. A sample of interest is digested in the solution at 90-95ºC 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 while diphenylcarbazide is oxidized to diphenylcarbazone. The Cr(III) and diphenylcarbazone further form a red-violet colored complex in the reaction.

The complex solution is measured quantitatively by a colorimeter or a spectrophotometer at 540 nm. 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 540 nm.

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 12.6.5 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.

12.2 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) 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..
g) 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.
h) New Jersey Department of Environmental Protection and Energy (NJDEPE). NJDEPE modified methods 3060/7196. 1992.
i) 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.
j) ASTM (American Society for Testing and Materials), 1981. Standard Practice for Oxidation Reduction Potential of Water. ASTM Designation:D1498-93.
k) 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.
l) U.S. Department of Health and Human Services - Agency for Toxic Substances and Disease Registry. Toxicological Profile for Chromium. April, 1993.
m) James, B.R., Petura, J.C., Vitale, R.J., and Mussoline, G.R. 1995. Hexavalent Chromium Extraction form Soils: A Comparison of Five Methods. Environ. Sci. Technol. 29:2377-2381.CD-ROM 3060A-10 Revision 1. December 1996
n) 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.
o) Certified reference material BCR-680 and BCR-681 (Cr in polyethylene)
p) Certified reference material BAM-S004 (glass containing hexavalent chromium)

12.3 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.

12.4 Apparatus / Equipment and Materials

12.4.1 Apparatus / Equipment

a) Vacuum filtration apparatus
b) Heating and stirring device: capable of maintaining the digestion solution at 90-95ºC 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 ±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 100ºC.

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.

12.4.2 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: hydrochlorid acid: H_2O, 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: borosilicated glass or quartz with a volume of 250 mL or equivalent.
e) Filter membranes (0.45 µm). Preferably cellulosic or polycarbonate membranes.

12.4.3 Reagents

a) Nitric acid: concentrated HNO3, analytical reagent grade or spectrograde quality. Store at 20-25ºC in the dark. Do not use concentrated HNO3 if it has a yellow tinge; this is indicative of photoreduction of NO3- to NO2, a reducing agent for Cr(VI).
b) Sodium carbonate: Na_2CO_3, anhydrous, analytical reagent grade. Store at 20-25ºC in a tightly sealed container.
c) Sodium hydroxide: NaOH, analytical reagent grade. Store at 20-25ºC in a tightly sealed container.
d) Magnesium chloride: $MgCl_2$ (anhydrous), analytical reagent grade. A mass of 400 mg $MgCl_2$ is approximately equivalent to 100 mg Mg^{2+}. Store at 20-25ºC in a tightly sealed container.
e) Phosphate Buffer:
    - K_2HPO_4 : analytical reagent grade.
    - KH_2PO_4: analytical reagent grade.
    - 0.5M K_2HPO_4 /0.5M KH_2PO_4 buffer at pH 7: Dissolve 87.09 K_2HPO_4 and 68.04 g KH_2PO_4 into 700 mL of reagent water. Transfer to a 1-L volumetric flask and dilute to volume.
b) Lead Chromate: PbCrO4, analytical reagent grade. Store at 20-25ºC in a tightly sealed container.
f) Digestion solution: Dissolve 20.0 ± 0.05 g NaOH and 30.0 ± 0.05 g Na_2CO_3 in reagent water in a 1-L volumetric flask and dilute to the mark. Store the solution in a tightly capped polyethylene bottle at 20-25ºC 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.
g) Potassium dichromate stock solution: Dissolve 141.4 mg of dried potassium dichromate, $K_2Cr_2O_7$ (analytical reagent grade), in reagent water and dilute to 1-L (1 mL=50 µg Cr).
h) Potassium dichromate standard solution: Dilute 10 mL potassium dichromate stock solution to 100 mL (1 mL=5 µg Cr).
i) Sulfuric acid, 10% (v/v): Dilute 10 mL of distilled reagent grade or spectrograde quality sulfuric acid, H_2SO_4, to 100 mL with reagent water.
j) Diphenylcarbazide solution: Dissolve 250 mg 1,5-diphenylcarbazide in 50 mL acetone. Store in a brown bottle. Discard when the solution becomes discolored.
k) Potassium dichromate, $K_2Cr_2O_7$, spiking solution (1000 mg/L Cr(VI)): Dissolve 2.829 g of dried (105ºC) $K_2Cr_2O_7$ in reagent water in a 1-L volumetric flask and dilute to the mark. Alternatively, a 1000 mg/L Cr(VI) certified primary standard solution can be used. Store at 20-25ºC in a tightly sealed container for use up to six months.
l) Potassium dichromate, $K_2Cr_2O_7$, matrix spiking solution (100 mg/L Cr(VI)): Add 10.0 mL of the 1000 mg Cr(VI)/L made from $K_2Cr_2O_7$ spiking solution (section 5.12) to a 100-mL volumetric flask and dilute to volume with reagent water. Mix well.
m) Acetone: analytical reagent grade: Avoid or redistill material that comes in containers with metal or metal-lined caps.
n) Reagent water - reagent water should be free of interferences.

12.5 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 4ºC until analysis.

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 should 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.

12.6 Test Procedure

12.6.1 Extraction

a) Take about 5 g of sample and measure its weight accurately to 0.1 mg. Place the sample into a clean suitable digestion vessel. Alternative sample amounts may also be used for samples with potentially very low or very high Cr (VI) concentrations.
b) For matrix recovery test, take another 5 g (or another 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 12.4.3.f or 12.4.3.l).
c) To each sample, add 50±1 mL of digestion solution (section 12.4.3.g) measured with a graduated cylinder. Also add approximately 400 mg of $MgCl_2$ (section 12.4.3.d) and 0.5 mL of 1.0 M phosphate buffer (section 12.4.3.e) to each sample. It is optional to add MgCl2 in the solution if the analytical techniques used can correct the oxidation/reduction of Cr. For polymer samples that appear to “float” on the surface of the digestion solution, 1-2 drops of a wetting agent (i.e. “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 90-95ºC, then maintain the samples at 90-95ºC 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 0.45 µm membrane filter. Rinse the inside of the filter flask and filter pad with reagent water and transfer the filtrate and the rinses to a clean 250-mL vessel. Keep the filtered solid on filter membranes for possible use in assessing low Cr (VI) matrix spike recoveries. Store the filtered solid at 4±2ºC.
f) With constant stirring, slowly add concentrated nitric acid solution to the 250 mL vessel dropwise. Adjust the pH of the solution to 7.5±0.5. Remove the stirring device and rinse, collecting the rinsate in the beaker. Transfer quantitatively the contents of the vessel to a 100-mL volumetric flask and adjust the sample volume to 100 mL with reagent water. Mix well. The sample digestates are now ready to be analyzed.

12.6.2 Color development and measurement

a) Transfer 95 mL of the extract to be tested to a clean 100-mL vessel. Add 2.0 mL diphenylcarbazide solution and mix. Slowly add H_2SO_4 solution to the vessel and adjust the pH of the solution to 2±0.5. Transfer quantitatively the contents of the vessel to a 100-mL volumetric flask and adjust the sample volume to 100-mL with reagent water. Let stand 5 to 10 minutes for full color development.
b) Transfer an appropriate portion of the solution to a 1-cm absorption cell and measure its absorbance at 540 nm with a colorimetric instrument.

c) Correct the absorbance reading of the sample by subtracting the absorbance of a blank carried through the color development procedures.
d) From the corrected absorbance, determine the mg/L of chromium present by reference to the calibration curve.

12.6.3 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 12.4.3.h) in measured volumes into a 10-mL volumetric flask to generate standard concentrations ranging from 0.1 to 5 mg/L Cr (VI) when diluted to the appropriate volume. 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 1 cm absorption cell and measure its absorbance at 540 nm 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).

12.6.4 Calculation of Analytical Results

a) Cr (VI) concentration (ppm) in total sample
    - Cr (VI) concentration = (A*D*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) Cr (VI) concentration (ppm) in coating layer
    - Cr (VI) concentration = (A*D*F)/L; where:
        i. A = Concentration observed in the digest (µg/mL)
        ii. D = Dilution factor
        iii. F = Final digest volume (mL)
        iv. L = Initial weight of coating layer in the sample (g)

c) Cr (VI) concentration (ppm) in chromate layer
    - Cr (VI) concentration = (A*D*F)/C; where:
        i. A = Concentration observed in the digest (µg/mL)
        ii. D = Dilution factor
        iii. F = Final digest volume (mL)
        iv. C = Total chromium weight in the coating layer of the sample (g)

Note: A simple “acid stripping” method can be used to dissolving the coating layer of the sample into diluted aqua regia solution or other acid solution. Dip sample in the diluted acid solution and take it out and check its appearance at about one minute intervals. The visual inspection should be able to tell if the coating layer is etched away. The weight of coating layer can be determined by measuring the sample weight before and after “acid stripping”. The total chromium weight in the coating layer can be determined by analyzing the acid stripping solution after the stripping test by ICP/AES or ICP/MS.

d) Relative Percent Difference
    a. RPD = {$|$ (S-D)/[(S+D)/2]} *100; where:
        i. S = Initial sample result (µg)
        ii. D = Duplicate sample result (µg)

e) Spike Recovery

a. Spike Percent Recovery = {(SSR-SR)/SA} *100; where:
    i. SSR = Spike sample result (µg)
    ii. SR = Unspiked sample result (µg)
    iii. SA = Spike added (µg)

12.6.5 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 12.4.3.l) or solid matrix spiking agent PbCrO4 (section 12.4.3.f) to spike into 50 mL of digestion solution (section 12.4.3.g) at a frequency of one each per batch of ≤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 ≤20%.

A soluble or insoluble pre-digestion matrix spike sample must be analyzed at a frequency of one each per batch of ≤20 samples. The soluble matrix spike sample is spiked with 1.0 mL of the matrix spiking solution (section 12.4.3.l) or at twice the sample concentration, whichever is greater. The insoluble matrix spike is prepared by adding 1-2 mg of $PbCrO_4$ (section 12.4.3.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 ≥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 ≤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.

12.7 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 IEC ACEC ad hoc Working Group.

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

13.1 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, 5.0 % nitric acid and 0.05 % potassium dichromate are recommended

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

a) 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.
b) All operation prior to instrument analysis must operate in the fume hood.
c) There should be a condenser to avoid the volatility under the condition.
d) When using the microwave oven, be strict to operate according to the directory of supplier.

13.2 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 of 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.

13.3 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.

13.4 Apparatus / Equipment and Materials

a) Scale: Precision level of 0.1 mg
b) Heating digester: equipped with vessels, reflux coolers and absorption vessels (for the digestion of metals and electronics)
c) Microwave sample preparation system: equipped with a sample holder and high-pressure PTFE-TFM 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)

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

13.5 Reagents

a) Water: Grade 1 specified in ISO 2696:1987 used for preparation and dilution of all sample solutions
b) Nitric acid: ρ(HNO3) =1.4 g/ml, 65 %, trace metal grade
c) Hydrochloric acid: ρ(HCl) = 1.16 g/ml, 37 %, trace metal grade
d) Potassium permanganate: G.R. 5% aqueous solution (w/v): Dissolve 5 g of potassium permanganate in 100ml of reagent water
e) Sodium chloride-hydroxylamine hydrochloride solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine hydrochloride in reagent water and dilute to100 mL
f) Tetrahydrofluoroborate solution: HBF4 50 %
g) Hydrogen peroxide: H2O2 (30%)
h) Sodium hydroxide: flakes: NaOH flakes
i) Sodiumtetraboro hydrate: NaBH4
j) Potassium borohydride, Sodium hydroxide, G.R. 1 % in 0.05 % NaOH: Add approximately 1000 ml of reagent water to a 1 L volumetric flask followed by the addition of 0.05 g sodium hydroxide. Add to 10.0 g potassium borohydride and stir to dissolve. Dilute it to scale with reagent water
k) Standard solution with 1000 µg/ml of mercury

13.5.1 Contaminations:

Contaminations can be a major source of error when working in the 10-9 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.

13.6 Sample Preparation

13.6.1 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.

13.6.2 Wet Digestion (Digestion of metal materials and electronics)

Common method for sample digestion
Approximately 1 g sample is weighed into the reaction vessel and 30 ml conc. HNO_3 is added. The vessel is furnished with a reflux cooler and an absorption vessel containing 10 ml 0.5 M HNO_3, before a temperature program is started to digest the samples for 1 h at room temperature and for 2 h at 90°C. After cooling to room temperature, the content of the absorption tube is put into the reaction vessel and the obtained solution is transferred into a 250 ml volumetric flask and filled up with 5 % HNO_3 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 0.45 µm filter and the solid residue is washed four times with 15 mL 5 % HNO_3. The obtained solution is transferred into a 250 mL volumetric flask and filled up with 5 % HNO_3 to the mark.

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.

Digestion of materials containing zirconium, hafnium, titanium, copper, silver, tantalum, niobium or tungsten
Approximately 1 g of the sample is weighed into a clean, dry reaction chamber and 20 ml of concentrated HCl, 10ml of concentrated HNO_3 are added. The vessel is furnished with a reflux cooler and an absorption vessel containing 10 ml 0.5 M HNO_3, before a temperature program is started to digest the samples for 15 min at 95°C $\pm$ 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 20 ml of reagent water and 15 ml of $KMnO_4$ solution to the reaction chamber. Mix thoroughly and continue heating for 30 min at 95°C $\pm$ 5°C. After cooling to room temperature the solution is quantitatively transferred over a filter into a 100 ml 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 250 ml volumetric flask. Add 6 mL of sodium chloride- hydroxylamine hydrochloride to reduce the excess permanganate. Dilute the digested sample solution to the mark with reagent water and mix thoroughly.

13.6.3 Microwave digestion with HNO3/HBF4/H2O2

About 100 mg of plastic material are weighed into a PTFE-TFM vessel. Five milliliters of conc. HNO3, 1.5 ml 50% HBF4 solution, 1.5 ml 30 % H2O2 and 1 ml 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 25 ml 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.: EDXRF) in order to confirm the absence of the target elements.

13.7 Test Procedure

13.7.1 Standard preparation / Stock solution preparation

ICP-AES (OES) and AFS: Prepare a working stock solution (10 mg/l) of mercury from a Certified Standard solution (1 ml of standard to 100 ml of solution), the concentration of which is 1000 mg/l. Mercury standards may be spiked with 1 - 2 drops of potassium permanganate (5 % KMnO4) for long storage.

CVAAS and ICP-MS:

a) Stock solution
b) The main stock solution contains 1000 µg/ml Hg. The use of commercially available concentrated standards for AAS is recommended.
c) Standard solution
d) 1 µg/ml Hg (in 1.5 % HNO3, stabilized by addition of a few drops of 5 % KMnO4 solution)
e) Aliquots of calibration: 100 µl, 200 µl, 500 µl
f) Corresponding to: 100 ng, 200 ng, 500 ng Hg
g) Diluent: 1.5% HNO3
h) Calibration volume: 10 mL
i) Reductant: 3 % NaBH4 in 1 % NaOH
j) Dissolve NaOH flakes and NaBH4 powder in deionized water and filter

Standards should be stored in inert plastic containers. Stock solutions of concentrations 1000 µg/ml or greater are usually stable for at least a year. Solutions of less than 1 µg/l 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 % KMnO4 solution.

13.7.2 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 (R2) is no less than 0.9995.
c) Calibrate the instrument with a calibration blank and insure that the result of the blank is lower than the method detection limit. If the calibration blank result is higher than MDL, check the instrument and the experiment process until the problem is solved.
d) Calibrate the instrument with three liquid standard solutions prepared from mercury standards, the calibration solutions range must cover no more than two orders of magnitude. If the analysis results exist in the range of ±10% of the real value, then the instrument is normal; otherwise repeat the analysis. If the analysis results still exceed ±10% of the real value, check the instrument until the problem is solved.

CVAAS
The standard calibration plot is established as follows:
Using suitable micro liter pipettes, 100 µL, 200 µL and 500 µL of standard solution (corresponding to the weight of 100 ng, 200 ng and 500 ng of mercury) are dispensed into 10 ml 1.5 % HNO3, the measurements are done and the calibration plot is set up.

13.7.3 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 ±10% of the real value, continue sample analysis; otherwise repeat the analysis. If the analysis results still exceed ±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 ±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 ±10 % of the real value, then recalibrate the instrument and reanalyze the previous ten samples.

13.7.4 Instrument parameters

CVAAS
a) Light source: Electrodeless discharge lamp or hollow cathode lamp
b) Wavelength: 253.7 nm
c) Spectral band width: 0.7 nm
d) Purge gas: N2 or Ar
e) Reduction agent: 3 % NaBH4 in 1 % NaOH

ICP-AES
a) Hg wavelength: 194.227 nm;
b) RF generator power: 1150 w;
c) Frequency: 27.12MHz;
d) Argon flow Carrier gas: 0.16 Mpa, Cool gas: 14 L/min, Auxiliary gas: 0.5 L/min;
e) Sample uptake rate: 1.6 mL/min.

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

AFS
a) Source: Hg hollow cathode lamp, Current: 30 mA, Wavelength: 253.7 nm;
b) Minus high-voltage: 360 V;
c) Oven temperature: 800°C;
d) Argon flow carrier gas: 600 ml/min, Screen gas: 1000 ml/min.
e) Reducing regent: Potassium borohydride.
f) Wash water: 6 % HNO3

13.7.5 Sample Analysis

a) 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 %.
b) 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.

CV-AAS
100 µl of the sample solution is given to 10 ml 1.5 % HNO3 and the measurement is done.

13.7.6 Calculation of Analytical Results

Data shall be analyzed using the following equation. Results shall be reported in mg/kg (i.e. µg/g).

ICP-AES

$$\text{Result} = \frac{\text{Instrument response (µg/ml)} \times \text{Sample solution volume (ml)} \times \text{Dilution factor}}{\text{Sample mass (g)}}$$

AFS and ICP-MS

$$\text{Result} = \frac{\text{Instrument response (ng/ml)} \times \text{Sample solution volume (ml)} \times \text{Dilution factor}}{1000 \times \text{Sample mass (g)}}$$

Note: Any serial dilution of sample must be included in the calculation.

CV AAS

$$\frac{V \cdot X}{A \cdot W} = concentration\ of\ metal\ in\ \mu g \cdot g^{-1}$$

where

V = total volume of the digestion solution in mL (250 mL for wet digestion, 25 mL for microwave digestion)
X = determined weight of metal in sample aliquot in µg
A = sample aliquot in mL (0.1 mL)
W = sample weight in g (1 g for wet digestion, 0.1 g for microwave digestion)

13.7.7 Test Report

The report should involve the following information:

a) The type and identification of the products tested
b) A reference to this standard, the used method (including digestion method and test instrument)
c) The results of the test expressed as milligrams / kilogram (“mg/kg”) in products tested
d) The detection limit or reporting limit
e) Any deviation, by agreement or otherwise, from the test procedure specified here
f) Date of the test and name of the operator
g) The detection limit

13.7.8 Quality Control

N.A.

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 ACEA ad hoc Working Group.

13.9 Annex

Table 12: 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	-

14 Determination of Lead and Cadmium in Polymer Materials 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 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.

14.2 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)

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 interfaces: 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.

14.4 Apparatus/Equipment and Materials

14.4.1 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 holder: Sample holder 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 0.1 mg
h) Glassware: All glassware shall be cleaned with 10% volume fraction nitric acid before use
    - Kjeldhal flask: 100 ml
    - Beakers: such as 100ml, 200ml, etc.
    - Volumetric flasks: Such as 50 ml, 100 ml, 200 ml etc.
    - Pipettes: Such as 1 ml, 5 ml, 10 ml, 20 ml, 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 µl, 100 µl, 200 µl, etc
m) Containers: For storage of standard solution and calibration standard
    - Containers made of high-density polyethylene to be used for ordinary measurement of element concentration. For determination on the ultratrace level, containers made of perfluoroalkoxy (PFA) or fluorinated ethylene-propylene copolymer (FEP). In either case, the user must confirm the suitability of the container selected.
n) Electric hot plate or heated sand bath
o) Muffle furnace: capable of being maintained 450 ± 25°C temperature.
p) Bunsen burner, or similar type of gas burner.
q) Microwave digestion system
    - Warning: 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 100 ml, etc.
s) Heat resistant thermal insulation board
t) Paper filter

14.5 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: ρ(H_2SO_4) = 1.84 g/ml, 95%
c) Nitric acid: ρ(HNO_3) = 1.40 g/ml, 65%
d) Hydrogen-peroxide: ρ (H_2O_2) = 1.10 g/ml, 30%
e) Hydrochloric acid:ρ (HCl) = 1.19 g/ml, 37%
f) Hydrofluoric acid: ρ(HF) = ISO 40 ≈ 42% ; JIS 46 ≈ 48%
g) Boric acid (HBO_3)
h) Standard solution with 1000 µg/l of lead
i) Standard solution with 1000 µg/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 µg/l.

WARNING: 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.

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.

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.

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

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

14.6 Sample Preparation

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. Generally it is advised to start with the highest amount of sample suitable for the choosen procedure. For further considerations see risks.

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

14.6.2 Preparation of test solution

Dry ashing method

When sample does not contain halogen compounds (Information may be available from previous screening experiments)

The sample is measured into a crucible mounted in the hole in the heat resistant thermal insulation board. The crucible is then heated gently with the burner in a hood for proper ventilation, taking care that the sample is not ignited. When the sample has decomposed to a charred mass, heating is gradually increased until the volatile decomposition products have been substantially expelled and a dry carbonaceous residue remains. The crucible and its contents are then transferred to the muffle furnace at 450 ± 25°C, with the door left slightly open to provide sufficient air to oxidize the carbon. Heating is continued until the carbon is completely oxidized and a clean ash is obtained. The crucible and its contents are then removed from the furnace and allowed to cool to ambient temperature. 5 ml of nitric acid are added, and the resulting solution is transferred to a 50 ml volumetric flask and filled up with water to 50 ml. The resulting solution is the concentrate sample solution. The concentrate sample solution may be diluted with water to the appropriate concentration level for each measurement apparatus. If an internal standard is to be used, it has to be added before filling up: for a final volume of 50 ml, internal standard of 500 µl for ICP-AES, and 500 nl for ICP-MS, respectively, has to be added before filling up.

When sample contains halogen compounds (Information may be available from previous screening experiments)

The sample is measured into a crucible. 10 to 15 ml of sulfuric acid are added, and the crucible and its contents are heated slowly on a hot plate or sand bath until the plastic melts and blackens. 5 ml of nitric acid are then added, and heating is continued until the plastic degrades completely and white fumes are generated.

After cooling, the crucible is placed in a muffle furnace maintained at 450 ± 25°C and the sample is evaporated, dried, and ashed until the carbon has been completely incinerated. After ashing, 5 ml of nitric acid are added, and the resulting solution is transferred to a 50 ml volumetric flask and filled up with water to 50 ml. The resulting solution is the concentrate sample solution. The concentrate sample solution may be diluted with water to the appropriate concentration level for each measurement apparatus. If an internal standard is to be used it has to be added before filling up: for a final volume of 50 ml, internal standard of 500 µl for ICP-AES, and 500 nl for ICP-MS, respectively has to be added before filling up.

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: EDXRF) in order to confirm the absence of the target elements.

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.

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

The sample is then allowed to cool down for several minutes. Hydrogen peroxide is added in small quantities, several milliliters at a time, and the sample is heated once again until white fumes are generated. After cooling, the solution is transferred to a 100 ml volumetric flask and the flask is then filled with water to 100 ml. The resulting solution is the concentrate sample solution. The concentrate sample solution may be diluted with water to the appropriate concentration level for each measurement apparatus. If an internal standard is to be used it has to be added before filling up: for a final volume of 100 ml, internal standard of 1000 µl for ICP-AES, and 1000 nl for ICP-MS, respectively, has to be added before filling up.

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

The sample is then allowed to cool for several minutes. Hydrogen peroxide is added in small quantities, several milliliters at a time, and the sample is heated once again until white fumes are generated. After cooling, the solution is transferred to a fluorocarbon resin vessel. 5 ml of hydrofluoric acid is added and the vessel is heated until white fumes are generated. Boric acid may be added to permit the complexation of fluoride for protection of the quartz plasma torch (in case no acid resistant sample holder is available). After cooling, the solution is transferred to a 100 ml volumetric flask and the flask is then filled with water to 100 ml. The resulting solution is the concentrate sample solution. The concentrate sample solution may be diluted with water to the appropriate concentration level for each measurement apparatus. If an internal standard is to be used it has to be added before filling up: for a final volume of 100 ml, internal standard (5.10) of 1000 µl for ICP-AES, and 1000 nl for ICP-MS, respectively, has to be added before filling up.
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: EDXRF) in order to confirm the absence of the target elements.

Closed system for acid decomposition
General decomposition method
The sample is measured into a microwave digestion vessel. 5 ml of nitric acid is added. The addition of hydrogen peroxide in small or catalytic quantities (such as 0.1 to 1 ml) may be performed as a support towards the complete oxidation of organic matter. The vessel is covered with a lid, and the vessel is placed in a microwave digestion device. The sample is digested in the microwave oven following a decomposition program specified in advance. After cooling, it is transferred to a 50 ml volumetric flask and the flask is then filled with water to 50 ml. The resulting solution is the concentrate sample solution. The concentrate sample solution may be diluted with water to the appropriate concentration level for each measurement apparatus. If an internal standard is to be used it has to be added before filling up: for a final volume of 50 ml, internal standard of 500 µl for ICP-AES, and 500 nl for ICP-MS, respectively has to be added before filling up.

Warning: 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.

When decomposition is inadequate or when the sample contains silica*, titanium*, etc. (Information may be available from previous screening experiments)
The sample is measured into a microwave digestion vessel. 5 ml of nitric acid and 1 ml of hydrofluoric acid are added. The addition of hydrogen peroxide in small or catalytic quantities (such as 0.1 to 1 ml) may be performed as a support towards the complete oxidation of organic matter. The vessel is covered with a lid, and the vessel is placed in a microwave digestion device. The sample is digested in the microwave oven following a decomposition program specified in advance. Boric acid may be added to permit the complexation of fluoride to protect the quartz plasma torch (in case no acid resistant sample holder is available). After cooling, the solution is transferred to a 50 ml volumetric flask and the flask is then filled with water to 50 ml. The resulting solution is the concentrate sample solution. The concentrate sample solution may be diluted with water to the appropriate concentration level for each measurement apparatus. If an internal standard is to be used it has to be added before filling up: for a final volume of 50 ml, internal standard of 500 µl for ICP-AES, and 500 nl for ICP-MS, respectively has to be added before filling up.

Warning:
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.

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: EDXRF) in order to confirm the absence of the target elements.

14.6.3 Preparation of laboratory reagent blank

Procedure identical to sample preparation is executed concurrently without sample.

14.7 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.

14.7.1 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 0-100 µg of each element are transferred to a 100 ml volumetric flask. Next, each reagent and – in the case of internal standard method - the appropriate amounts of the solvents for the internal standard solutions are added to achieve reagent concentrations identical to those present in the sample solution. The resulting solution is the mixed calibration standard solution.

14.7.2 Development of calibration curve

The spectrometers are prepared for quantification. Some of the solution obtained in 14.7.1 is nebulized into the argon plasma or by acetylene/air flame, respectively. A hydrofluoric acid resistant sample holder has to be used when the sample solution contains hydrofluoric acid.

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 the annex, table 13.

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 the annex, table 14.

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 the annex, 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.

14.7.3 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.

14.7.4 Calculation

The concentration measured in 14.7.3 is the concentration of each element in the sample solution. The concentration of each element in the sample is calculated from the equation:

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

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.

14.7.5 Test Report

As a minimum, the following items must be included in the test report:

a) a reference to this International Standard
b) a reference to the method used;
c) complete identification of the sample
d) the results of the determinations
e) any details not specified in this International Standard or which are optional, as well as any factors which may have affected the results.

14.7.6 Quality Control

N.A.

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 ACEC ad hoc Working Group.

14.9 Annex

14.9.1 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)

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 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

14.9.3 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

15 Determination of Lead and Cadmium in Metallic Materials by ICP-AES, ICP-MS, and AAS

15.1 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-precipation) 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.

15.2 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

15.3 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.

15.4 Apparatus/Equipment and Materials

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

15.5 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: ρ(HCl) = 1.16 g/ml
c) Nitric acid: ρ(HNO3) = 1.4 g/ml
d) Nitric acid: Dilution (1+ 2): Dilute 1 volume of concentrated nitric acid (5.3) with 2 volumes of water (5.1).
e) Perchloric acid: ρ(HClO4) =1.67 g/ml, 70%
f) Phosphoric acid: ρ(H3PO4) =1.69 g/ml, more than 85%
g) Sulfuric acid: ρ(H2SO4) = 1.84 g/ml
h) Sulfuric acid: Dilution (1+1): Dilute 1 volume of concentrated sulfuric acid (5.7) with 2 volumes of water (5.1).
i) Hydrofluoric acid: ρ(HF) = ISO 40～42%、JIS 46～48%
j) Hydrobromic acid: ρ(HBr) = 1.48 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 µg/l of lead
o) Standard solution with 1000 µg/l of cadmium
p) Internal standard solution
    - Internal standard elements that do not interfere with the target element will be used. Also, the presence of these internal standard elements in the sample solution must be at negligible levels. Sc, In, Tb, Lu, Re, Rh, Bi and Y may be used as internal standard elements.

WARNING
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.

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.

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.

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

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

15.6 Sample Preparation

15.6.1 Test portion

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

15.6.2 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 loosing 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.

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

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

If containing tin
A beaker containing the sample is covered with a watch glass. 10 ml of mixed acid 3 is added in small quantities. After violent reaction ends, the beaker is heated slowly until the sample is dissolved completely. After cooling, the underside of the watch glass and inside wall of the beaker are rinsed with water, and the watch glass is removed. 10 ml of sulfuric acid is added and the beaker is heated until white fumes of SO3 are liberated. After cooling for several minutes, 20 ml of hydrobromic acid are added, and the beaker is heated until white fumes are visible. This process is repeated three times. After cooling to room temperature, 10 ml of nitric acid is added to dissolve salts. After cooling to room temperature, the solution is transferred to a 100 ml volumetric flask which is then filled with water to 100 ml. The resulting solution is the concentrate sample solution. The concentrate sample solution is diluted with water to the appropriate concentration level for each measurement apparatus. If necessary, an internal standard element, rhodium, for example, is added to the flask before filling with water. The type of element and its amount depend on the analytical method selected. The particular paths of dilution have to be taken into account in the calculation of results. Both, dilution and internal standard addition have to be documented in the test report.

15.6.3 Preparation of laboratory reagent blank

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

15.7 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 – 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.

15.7.1 Preparation of calibration standard

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 µg of each element are transferred to a 100 ml 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.

Internal standard method
Calibration blank and three calibration standards are prepared as calibration solutions.
Each standard element solution is added in steps in 100 ml measuring flasks. In order to achieve concentrations equivalent to that of the sample solution, reagents and internal standard elements are added to prepare mixed calibration standard solutions.

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

15.7.2 Measurement of calibration standard

ICP/AES(-OES)
Some part of the calibration solutions prepared as described in 15.7.1 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 the annex, table 16. 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.

ICP/MS
The ICP mass spectrometer is prepared for quantification. Some of the solution obtained in 15.7.1 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 17.

AAS
Portions of the calibration solutions prepared as described in 15.7.1 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 18. 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.

15.7.3 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.

15.7.4 Calculation

The spectrometer readings of each sample as obtained according to 7.3 and the calibration curve developed as described in 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:

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

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

15.7.5 Test Report

As a minimum, the items to be included in the test report are:

a) a reference to this International Standard
b) a reference to the method used; describing the individual procedure taken
c) complete identification of the sample
d) the results of the determinations
e) any details not specified in this International Standard or which are optional, as well as any factors which may have affected the results.

15.7.6 Quality Control

N.A.

15.8 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 ACEA ad hoc Working Group.

15.9 Annex

15.9.1 ICP/AES(-OES)

Table 16: 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)

15.9.2 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 17: 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

15.9.3 AAS

Recommended measurement wavelengths for AAS.

Table 18: 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

16 Determination of Lead and Cadmium in Electronics by ICP-AES, ICP-MS, and AAS

16.1 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 with a maximum grain size of 250 µm. The powder is either digested with aqua regia or microwave-enhanced with HNO3, HBF4, H2O2 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.

16.2 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.

16.3 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 interfaces: 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).

16.4 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 40 mL.

CAUTION: There are many safety and operational recommendations specific to the model and manufacturer of the microwave equipment used in individual laboratories. The analyst was required to

consult the specific equipment manual, manufacturer, and literature for proper and safe operation of the microwave equipment and vessels.

i) Scale: Precision level of 0.1 mg
j) Glassware: All glassware shall be cleaned with 10% volume fraction nitric acid before use
    - Beakers: Such as 100 ml, 200 ml, 500 ml, etc.
    - Volumetric flasks: Such as 100 ml, 200 ml, 500 ml, etc
    - Pipette: Such as 1 ml, 5 ml, 10 ml, 20 ml, etc.
    - Graduated cylinder
    - Watch glass
k) Micropipette: Such as 200 µl, 500 µl, 1000 µl, etc.
l) PTFE/PFA containers: All equipment shall be cleaned with 10% volume fraction nitric acid before use
    - Beakers: Such as 100 ml, 200 ml, 500 ml, etc.
    - Volumetric flasks: Such as 100 ml, 200 ml, 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 40 ml, 100lml, etc.
p) Filter:
    - Glass fiber filter 0.45 µm (digestion with aqua regia)
    - Whatman filter 0.45 µm (microwave digestion)

16.5 Reagents

a) Water: Grade 1 specified in ISO 3696:1987 used for preparation and dilution of all sample solutions
b) Hydrochloric acid: ρ(HCl) = 1.16 g/ml, 37 %
c) Hydrochloric acid: Dilution (1+ 5): One part hydrochloric acid (5.2) diluted with two parts water (5.1).
d) Nitric acid: ρ(HNO3) =1.4 g/ml, 65 %
e) Mixed acid (3 parts hydrochloric acid and 1 part nitric acid)
f) Tetrafluoroborate solution, HBF4, 50 %
g) Hydrogen peroxide H2O2, 30 %, p.a. grade
h) Standard solution with 1000 µg/g of lead
i) Standard solution with 1000 µg/g of cadmium
j) Standard solution with 10000 µg/g of cupper
k) Standard solution with 10000 µg/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.

WARNING
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.

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.

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.

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

16.6 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 loosing some of the target analyte. Samples should be dissolved completely without any remains under heating at high temperatures.

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

16.6.1 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.

16.6.2 Digestion with aqua regia

Approximately 2 g of the ground sample (maximum grain size: 250 µm) is weighed into the reaction vessel and 22.5 ml conc. HCl and 7.5 ml conc. HNO3 are added. The vessel is furnished with a reflux cooler and an absorption vessel containing 10 mL 0.5 M HNO3, 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 15 ml 5 % HCl. The obtained solution is transferred into a 250 ml 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 100 ml, internal standard of 1000 µl for ICP-AES, and 1000 nl for ICP-MS, respectively, has to be added before filling up.

If there are sample remnants on the filter, they have to be checked by appropriate measurements (e.g: 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 HNO3) is added and the beaker is heated for 2 hours at 120°C and then allowed to stand for 12 hours at room temperature. The underside of the watch glass and inside wall of the beaker are rinsed with water, and the watch glass is removed. After cooling, the sample is filtered with a 0.45 µm membrane filter. The remnants are rinsed with hydrochloric acid. The solution is transferred to a volumetric flask and the flask is filled with water. The resulting solution is used for further measurements.

16.6.3 Microwave digestion

300 mg of ground sample (maximum grain size: 250 µm) is weighed into a PTFE-TFE or a PTFE/PFA vessel. 4 ml of nitric acid, 2 ml of tetrafluoroborate, 1 ml of hydrogen peroxide and 1 ml of water are added. The vessels are agitated carefully for approximately 10 s before sealing to allow the escape of immediately formed gases. The sample is then digested in a microwave oven following a digestion program specified in advance. During these digestion step A, organic components such as 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 4 ml 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 the annex (Table 19).

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 25 ml 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: EDXRF) 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.

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

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

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

16.7 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.

NOTES – To increase the reliability of the test method, the standard-additions method may be used.

NOTES – 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.

16.7.1 Preparation of calibration solution

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 µg of each element are transferred to a 100 ml volumetric flask. For matrix matching method, a close matrix matching of standard solution is necessitated. The matrix elements are identified by previous EDXRF 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.

Internal standard method
Calibration blank and three calibration standards are prepared as calibration solutions.

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

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

ICP/AES, AAS
The high iron and copper content necessitates a close matrix matching of standard solutions and an appropriate line selection (Reference d). Therefore the calibration should be done using matrix adjusted calibration solutions. Recommended wavelengths can be found in the annex.

ICP/MS
Here the use of an appropriate internal standard is recommended. The annex gives the best m/z for the measurements together with potential interferences.

16.7.2 Standard preparation

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.

Aqua regia digestion standards
Calibration blank: 10% HCl
Calibration standards 1 to 3 (100 ml in each case): Solutions containing 1500 µg/ml Fe and 1500 µg/ml Cu, 24 ml HCl 37% and target elements Pb and Cd in different concentrations. 1.0 µg/ml target element in solution corresponds to 125 µg/g target element in electronics.

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

ICP/MS
Calibration blank and three calibration standards are prepared as calibration solutions.

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

16.7.3 Calibration

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.

ICP/MS
The ICP mass spectrometer is prepared for quantification. Some of the solution obtained in 16.7.1 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 holder has to be used when the sample contains tetrafluoroborate.

16.7.4 Development of calibration curve

ICP/AES(-OES)
Some part of the calibration solutions prepared as described in 16.7.1 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 Table 20. 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.

ICP/MS
The ICP mass spectrometer is prepared for quantification. Some of the solution obtained in 16.7.1 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 Annex, Table 21.

AAS
Portions of the calibration solutions prepared as described in 16.7.1 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 Annex (Table 22). 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.

16.7.5 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.

16.7.6 Calculation of Analytical Results

The spectrometer readings of each sample as obtained according to 7.3 and the calibration curve developed as described in 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:

Lead or cadmium μg /g= (A1 – A2) V / m (Eq. 1)*

where A1 is concentration of each target element in the test sample solution in μg/ml; A2, the concentration of each target element in the laboratory reagent blank in μg/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.

16.7.7 Test Report

As a minimum, the items to be included in the test report are:

a) a reference to this International Standard
b) a reference to the method used; describing the individual procedure taken
c) complete identification of the sample
d) the results of the determinations
e) any details not specified in this International Standard or which are optional, as well as any factors which may have affected the results.

16.7.8 Quality Control

N.A.

16.8 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 ACEC ad hoc Working Group.

16.9 Annex

Table 19: 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

16.9.1 ICP/AES(-OES)

Table 20: Recommended wavelengths and interfering elements

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)

16.9.2 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 21: 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

16.9.3 AAS

Recommended measurement wavelengths for AAS

Table 22: 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

17 Reference Methods and Materials

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

Table 23: 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