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

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Abstract
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 the European Union (EU) directive on the "Reduction of certain Hazardous Substances in electrical and electronic equipment" (RoHS), in Chinese draft legislation and in the US (California) Electronic Waste Recycling Act of 2003. 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. 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 the work by the IEC (International Electrotechnical Commission) TC (Technical Committee) 111 "Environment" WG (Working Group) 3 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.

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 standard 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.

Scope

This document provides test procedures for determining the levels of Lead (Pb), Mercury (Hg), Cadmium (Cd), hexavalent Chromium (Cr VI), and two types of brominated flame retardants, Polybrominated Biphenyls (PBB) and Polybrominated Diphenyl Ethers (PBDE) contained in electrotechnical products.

Examples of categories of electrotechnical products are:

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

This document will not determine:

- Definition of a "unit" or "homogenous material" as the sample
- Disassembly procedure to get to a sample
- Assessment procedures
- Test Procedure Overview

Test Procedure Scope

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

- Analytical test procedures
- Laboratory implementation

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

The analytical test procedures step can itself be divided into seven important points:

- Scope, application and summary of method
- References, normative references, reference methods and reference materials
- Terms and definitions
- Apparatus / Equipment and materials
- Reagents
- Sample preparation

- Test procedure, which includes:
  - Calibration
  - Instrument performance
  - Sample analysis
  - Calculation of analytical results
  - Test report
  - Quality control

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

Individual test procedure descriptions in the standard follow this seven point outline.

The laboratory implementation will not be covered in this document, as labs should be able to implement the test procedures described using procedures and standards addressed in other sources. The implementation step includes suitable quality assurance measures and a validation protocol that documents the performance of the analytical method using the instrument in the lab. Quality assurance systems such as Good Laboratory Practice (GLP) and/or accreditation to similar (inter-) national systems (e.g. IEC/ISO 17025) are strongly encouraged.

Sample
This document refers to the “sample” as the object to be processed and measured according to the procedures following below to determine the levels of the six regulated substances. A sample can either be a polymer material, a metallic material or electronics (e.g. in form of populated PWBs or components).

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

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

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

The entity can also decide to prepare a sample which is a on the component level. For this kind of sample the procedures offered for electronics are especially suited.

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

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

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

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

Test Procedure Flow

The Figure 1 below describes the flow for the test procedure to determine the levels of regulated substances in electro-technical products.

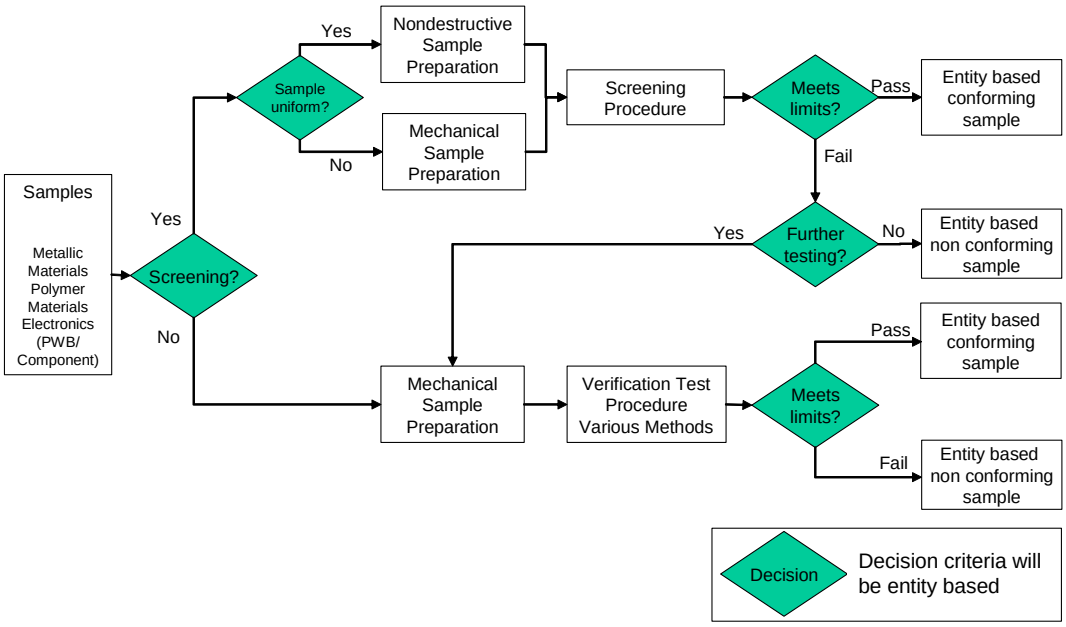

Figure 1 - Flowchart of the Test Procedure

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

Screening by XRF Spectroscopy

The screening of a sample is performed using any XRF spectrometer, providing it has the performance characteristics described in this method. It must be noted that the screening test procedure should be performed under controlled conditions. The XRF analysis technique has limitations to its use and the applicability of the results obtained, although it's fast and resource efficient way of analysis has its merits particularly for the demands of the electro-technical industry.

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

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

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

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

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

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

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.

Verification Test Procedure

The verification test procedure is performed after a mechanical sample preparation using a variety of analytical procedures tailored to the regulated substances and the material of the sample, which can be either polymer materials, metallic materials or electronics(in form of populated PWBs or components). Table 1 gives an overview of the verification methods, which are described in detail in chapter 7 to 14. The intent of using a particular verification test procedure is to ensure the most accurate results possible; however, it most likely will take more resources to carry out. After the verification test procedure it can be decided if the sample meets the limits based on the entity's criteria for regulated substances.

Table 1 - Overview of the Content of the Verification Test Procedure

Steps	Substances	Polymer Materials	Metal Materials	Electronics (PWBs/Components)
Mechanical sample preparation (Chapter 5)		Direct measurement Grinding	Direct measurement Grinding	Grinding
Chemical sample preparation		Microwave digestion Acid digestion Dry Ashing Solvent extraction	Acid digestion	Microwave digestion Acid digestion Solvent extraction
Analytical technique definition (incl. typical margins of errors)	PBB/PBDE	GC/MS (Chapter 7) HPLC/UV (Chapter 8)	NA	GC/MS (Chapter 7) HPLC/UV (Chapter 8)
	Cr VI	Alkaline Digestion/ Colorimetric Method (Chapter 10)	Spot-test procedure/ boiling-water-extraction procedure (Chapter 9)	Alkaline Digestion/ Colorimetric Method (Chapter 10)
	Hg	ICP-AES, ICP-MS, CV AAS, AFS (Chapter 11)		
	Pb/Cd	ICP-AES, ICP-MS, AAS (Chapter 12)	ICP-AES, ICP-MS, AAS (Chapter 13)	ICP-AES, ICP-MS, AAS (Chapter 14)

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.

Reference Methods and Materials

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

Commercially Available Reference Materials (CRM)

There exist a variety of commercially available reference materials, mainly in polymeric and metallic matrices, but also, to a lesser degree, in glass and ceramic matrices. These materials have been specially formulated (doped) with the five elements of concern (Pb, Cd, Hg, Cr and Br), possibly with other elements present as well. These doped materials were then analyzed using a variety of wet chemistry methods, at a number of testing laboratories, to determine the concentration of these elements. Table 2 gives an overview over existing CRMs suited for regulated substances in electrotechnical products.

Table 2 - 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

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.

Documents

The Committee Draft (CD) on "Procedures for the Determination of Levels of Regulated Substances in Electrotechnical Products" has been issued in June 2005.[5] This draft can be obtained by downloading it from the IEC TC 111 website, contacting the relevant National Committee (NC) or the author.

The CD addresses and incorporates the comments received by the National Committees and a multitude of other stakeholders. To understand how the comments have been addressed, an additional document has been prepared (111_25e_INF.pdf),[6] which lists all comments received and the action taken by the WG 3.

Timeline

The next draft (Committee Draft for Voting, CDV), which will include comments received from a variety of stakeholders and from an ongoing international interlaboratory study is expected to be released in December 2005. National Committees will vote on this draft and it is expected that the Final Draft International Standard (FDIS) will be available by July 2006. The printed final standard is expected then for October 2006. This is in line with the current timeline of the European RoHS, which takes effect in July 2006.

Literature

1. Reduction of certain Hazardous Substances in electrical and electronic equipment (RoHS)
2. Management Methods on the Prevention and Control of Pollution Caused by Electronic information Products
3. US (California) Electronic Waste Recycling Act of 2003 (S.B. 20)
4. US (California) Electronic Waste, Advanced Disposal Fees (S.B. 50)
5. Procedures for the Determination of Levels of Six Regulated Substances (Lead, Mercury, Hexavalent Chromium, Polybrominated Biphenyls, Polybrominated Biphenyl Ether) in Electrotechnical Products, IEC Project number: IEC 62321, Ed.1, 111_24e_CD.pdf, June 2005
6. Revised compilation of comments containing the decisions taken by the WG3, 111_25e_INF.pdf, June 2005