



STG - Systems

STG RoHS Analysis Guideline
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Desk Procedure Description

Body

1.0 Scope

This document provides RoHS testing guideline for determining if Lead (Pb), Mercury (Hg), Cadmium (Cd), Hexavalent Chromium (Cr(VI)), and two types of IBM banned brominated flame retardants, polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE) are contained in electrotechnical products, and if so their levels.

2.0 Determination of Cd, Pb, and Hg

RoHS Determination of Cd, Pb, and Hg in Metallic and Polymeric Samples

Determination of Cd, Pb, and Hg in Metallic Samples

2.1 Metal Samples

The determination of Cd, Pb, and Hg in metals is accomplished by dissolving the sample in appropriate acids followed by analysis by ICP/AES, ICP/MS, AAS, or some other suitably sensitive technique. The wide variety of metallic samples and the choice of appropriate acids is beyond the scope of this procedure. In general, nitric and hydrochloric acids should be the first choice for most samples. For more unusual samples the use of sulfuric acid, phosphoric acid, hydrofluoric acid, and fluoroboric acid may be required. In all cases, however, there must be no residual precipitates or undissolved sample remaining.

Determination of Cd, Pb, and Hg in Polymeric Samples

2.2 Approach

The determination of Mercury, Hg, in a polymeric sample is to be done by Direct Mercury Analysis (e.g. Milestone Inc) following EPA Method 7473 "Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry." Additionally, Milestone Application Note HG-19 "Determination of Mercury in Plastic" provides procedural guidance. No additional tests need to be done, however, a mercury-containing plastic quality control sample should be run on a regular basis to insure quality.

The determination of Cadmium, Cd, and Lead, Pb, in a polymeric sample is to be done by two procedures. First, a quantitative procedure such as EN1122 is to be performed in which the sample is milled to a fine consistency and digested with acid. This procedure demands a choice of acids which depends upon the polymer. For example, polyethylene, polypropylene, polyvinyl chloride need to use a combination of sulfuric acid, hydrogen peroxide, and nitric acid in order to be effective, while nylons may generally be decomposed by nitric acid alone. Alternatively, a quantitative dry ashing procedure may be used, however, low results can be obtained for certain polymers unless the furnace is slowly programmed to avoid flaming and loss of volatiles. Regardless of which quantitative procedure is chosen, a second semi-quantitative procedure (XRF) must be used to confirm the quantitative results. This redundancy in testing serves to provide additional confidence in testing results. The quantitative dry ashing/acid digestion procedure is described below. In all cases both tests need to be performed. XRF test results are usually only semi-quantitative since standards made from the same matrix as the sample are usually unavailable. For this reason detection of any Cd or Pb in a sample should result in the sample being considered a non-compliant sample, regardless of the number generated by the XRF. A sample is only considered compliant when it passes both the quantitative dry ashing test and the XRF test.

If the quantitative procedure results in a number which is non-compliant or the XRF detects Cd or Pb, the sample is non-compliant.

2.3 Dry Ashing Method Summary (for Cd and Pb)

Polymeric samples are dry ashed in a muffle furnace followed by a nitric acid digestion of the ash. This extract is diluted as necessary and analyzed by ICP/AES, ICP/MS, or AAS for cadmium and lead content.

Procedure:

Ashing - A suitable amount of sample, generally 0.2g to 1.0g, is weighed to the nearest 0.1mg, and placed into a porcelain crucible. This crucible is placed into a programmable muffle furnace initially set at 200C and slowly ramped to 460C. A crucible cover placed on top slightly offset so that vapors can escape. The crucible cover should be removed after charring to allow better oxidation of the sample. The duration in the muffle furnace is typically 3-4 hours, but ultimately depends on the sample. If the sample or the crucible appear to have carbonaceous matter on any of the surfaces, the time should be extended until this material is completely oxidized/vaporized. Once all the carbonaceous material is gone, the crucibles may be removed from the muffle furnace and allowed to cool.

Acid Digestion – Ten milliliters of concentrated nitric acid is added to the ashed remains in each crucible and the crucible heated on a hotplate or digestion block at 90-100C. One hour is typically sufficient for this step. The crucibles are then removed from heat and allowed to cool. The contents are then quantitatively transferred to polypropylene or glass container and the volume brought to 50 milliliters (20 milliliters may be more appropriate if low levels of Cd and Pb are expected). The samples may have to be filtered at this point to remove suspended particles if they are present.

Analysis – The digest may be analyzed with any of the common analytical techniques such as AAS, ICP/AES, or ICP/MS. Samples should be diluted as appropriate to maintain Cd and Pb concentrations within the instrument calibration range.

Calculations – The Cd and Pb concentration values (in ug/ml) should be multiplied by any dilution factors (if used) and by the volume (in ml) of solution in the initial container. This value represents the amount (in micrograms) of the Cd and Pb present in the sample, and should be divided by the sample weight (in grams) to arrive at a concentration value in ppm units.

3.0 Determination of PBB and PBDE in Polymeric Materials

Determination of Polybrominated Biphenyl (PBB) and Polybrominated Diphenyl Ether (PBDE) in Polymeric Materials

3.1 Scope

This document describes the methodology for verifying IBM suppliers' material declaration on compliance to two classes of IBM banned brominated flame retardants (BFRs): polybrominated biphenyl (PBB) and polybrominated diphenyl ether (PBDE). This ban applies to all 209 congeners of PBBs and all 209 congeners of PBDEs, including decabromodiphenyl ether (BDE-209) which is currently exempted by EU RoHS. Any detectable levels of these two classes of BFRs, even though below EU RoHS allowable limit, are considered noncompliant to IBM specification.

3.2 Approach

A fast and simple qualitative analysis by X-ray Fluorescence (XRF) can be performed to determine if bromine (Br) is present in the homogeneous polymer. If the presence of Br is confirmed by XRF, further information should be obtained from the supplier on the specific brominated flame retardant (BFR) used in the material; not all BFRs are banned by IBM.

For analysis of PBBs and PBDEs in a homogeneous polymer, a soxhlet extraction followed by Gas Chromatography-Mass Spectrometry (GC/MS) shall be employed to determine if any of the PBB or PBDE congeners are present in the homogeneous polymer matrix. Optionally, a 16 hour room temperature extraction followed by GC/MS (SIM mode) analysis can be performed as a preliminary screen test. If PBB or PBDE congeners are detected in the screen test, the polymer is considered noncompliant. If the screen test is negative for PBBs or PBDEs, a soxhlet extraction followed by GC/MS shall be performed to determine compliance.

In general, the solubility of the polymer matrix and the particle size of the sample matrix greatly influence the extraction efficiency, and thus, the proper detection of PBBs/PBDEs for compliance. Therefore, appropriate extraction solvent(s) and sample grinding (500 um particle size, especially for partially soluble and insoluble polymer matrixes) prior to analysis are crucial for accurate testing.

3.3 Additional Equipment

A grinding instrument capable of reducing sample to a size of 500 um or smaller.

3.4 Procedure

The general procedure recommended by BAM "Determination of Pentabromination Diphenylethers and Octabrominated Diphenylether in Polymers" shall be followed with the following additions:

- 1) Samples are ground to a size of 500 um or smaller before extraction
- 2) Depending on the type of polymer, appropriate solvent(s) should be used to dissolve the polymer matrix. If the nature of the polymer is unknown, toluene should be used as universal solvent. For specific polymers, the following solvents should be used:

- Toluene for ABS, HIPS and PC/ABS
- Propanol for Polyamides and Polyesters
- 5/25 Dichloromethane/cyclohexane for Polyolefins

3) The analysis of PBBs and PBDEs is carried out in SIM (Single Ion Monitoring) mode with the mass traces given in tables below:

Reference masses for the quantification of PBBs

	Ions monitored in the extract		
Mono-BB	231.9	233.9	
Di-BB	309.8	311.8	<u>313.8</u>
Tri-BB	387.8	389.8	<u>391.8</u>
Tetra-BB	307.8	309.8	<u>467.7</u>
Penta-BB	385.7	387.7	<u>545.6</u>
Hexa-BB	465.6	467.6	<u>627.5</u>
Hepta-BB	543.6	545.6	<u>705.4</u>
Octa-BB	623.5	625.5	<u>627.5</u>
Nona-BB	701.4	703.4	<u>705.4</u> (863.4)
Deca-BB	781.3	783.3	<u>785.3</u> (943.1, 215.8, 382.6, 384.5)

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

Reference masses for the quantification of PBDEs

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

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

References

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Long Description

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