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SJ

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SJ/T 11365-2006

Testing Methods for Hazardous Substances in Electronic Information Products

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Contents

Preface

This standard is modified in relation to IEC 111/54/CDV "Procedures for the Determination of Levels of Six Toxic Substances (Lead, Mercury, Cadmium , Hexavalent Chromium, Polybrominated Biphenyls, Polybrominated Diphenyl Ethers) in Electronic Information Products".

Annex A of this standard is normative.

This Standard was proposed by the Information Industry Products Pollution Prevention Working Group of the Ministry of Information Industry.

This Standard is under the jurisdiction of China Electronics Standardization Institute.

This standard is mainly drafted by: the China Ceprei Laboratory, the 5th Electronics Research Institute of the Ministry of Information Industry of China, SGS -CSTC Standards Technical Services Co., Ltd, Shanghai Intertex Testing Service Ltd. , Agilent Technologies Inc., Beijing Pony Center for Physical and Chemical Analysis, Shenzhen Centre Testing International, Special Materials Testing Centre of the Ministry of Information Technology, and Huawei Technologies Co., Ltd.

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The Electronic Products Pollution Prevention Standards Working Group of the Ministry of Information Technology is responsible for the interpretation of this Standard.

Introduction

Currently, there still are large amounts of hazardous substances and elements, such as lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls and polybrominated diphenyl ethers in electronic information products because of function, performance and process requirements. The improper disposal of electronic information products containing these hazardous substances or elements may result not only in pollution of the environment, but also waste of resources. Therefore, in order to save resources and protect the environment, pollution control in electronic information products by reducing and substituting hazardous substances and elements has been made a major task of the public authorities. For this reason, under the principle of "beginning from the source and legislation going ahead", the Ministry of Information Industry, together with six other ministries and commissions prepared the Measures for Administration of the Pollution Control of Electronic Information Products (Decree No.39 of the Ministry, hereinafter referred as "the Measures") to promote pollution control in electronic information products through legislation, which serves to limit and inhibit the use of these hazardous substances and elements at different stages, such as the development, design, production, distribution, and import, of electronic information products.

To further implement the Measures and achieve the target of limiting the use of hazardous substances or elements in electronic information products, corresponding unified testing method standards must be employed. Therefore, this standard has been formulated to work with the implementation of the *Measures,* and to provide uniformity in the methods of testing for the six hazardous substances in electronic information products, lead (Pb), cadmium (Cd), hexavalent chromium [Cr (VI)], mercury (Hg), polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs).

SJ/T 11365-2006

Testing Methods for Hazardous Substances in Electronic Information Products

1. Scope

This Standard specifies the method of testing for six hazardous substances or elements, namely lead (Pb), cadmium (Cd), hexavalent chromium (Cr VI), mercury (Hg), polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs), in electronic information products.

This Standard applies to the electronic information products (EIPs) defined by the *Measures*.

2. Normative references

The following document contains provisions which, through reference in this text, constitute provisions of this Standard. At the time of publication, the edition was valid. All standards are subject to revision, and users are encouraged to investigate the possibility of using the most recent editions of the standard indicated below.

SJ/T 11363-2006, *Requirements for Concentration Limits for Certain Hazardous Substances in Electronic Information Products*

See Sections 5 and 8 for other cited documents.

3. Terms and Definitions

The following terms and definitions are employed in this Standard.

3.1 Electronic Information Products (EIPs)
Electronic radar products, electronic communication products, television broadcasting products, computer products, domestic electronic appliances, electronic measuring instruments, specialized electronic products, electronic component products, electronic applications products and electronics materials products and combinations thereof are manufactured through the use of electronic technology

3.2 Substance
Elements or compounds occurring in nature

3.3 Screening
An analytical approach with the primary goal of quantifying the concentration of a target element in a tested material

3.4 Polymer materials
A range of synthetic or semi-synthetic organic condensation or polymerization products that can be moulded or extruded into films or objects in other forms.
Note: Polymer materials include polyethylene, polyvinyl chloride, epoxy resin, polyamide, polycarbonate, ABS resin and polystyrene etc.

3.5 Metallic materials
Elements or mixtures of metallic elements, including all ferrous, non–ferrous or alloy materials
Note: Metallic materials may be iron alloys, nickel alloys, tin alloys, aluminium alloys, magnesium alloys, copper alloys, zinc alloys or precious metal alloys etc.

3.6 Special electronic materials
Certain special materials that are used in electronic information products, which are mixtures of two or more of metallic materials, organic materials and inorganic non-metallic materials
Note: Special materials may be circuit board substrates, conducting adhesives, and semiconducting functional materials

3.7 Inorganic non-metallic materials
Materials consisting of oxides, carbides, nitrides, borides and silicates, aluminates, phosphates and borates of certain elements. A general term for materials excluding polymeric and metallic materials
Note: Inorganic non-metallic materials may be glasses and ceramics etc

3.8 Matrix
The material or substance in which the analyte is contained or embedded.

3.9 Homogeneous materials
Materials made from one or more substances uniformly distributed throughout

3.10 Test unit
A sample that can be submitted for testing without the need for further mechanical dismantling

3.11 X-ray fluorescence spectrum (XRF)
A method in which a beam of X-ray or low energy rays is used to irradiate a test sample to induce the emission of characteristic X-rays for qualitative or quantitative analysis. It can be classified into wavelength-dispersive X-ray fluorescence and energy-dispersive X-ray fluorescence according to the methods of excitation, dispersion, and detection.

3.12 Wavelength-dispersive X-ray fluorescence (WD-XRF)
The atoms of the elements to be measured in the sample are subjected to high energy radiation and inner electron transition is induced to emit X-rays with certain energy levels and at characteristic wavelengths. The elements to be analysed are measured qualitatively and quantitatively by the obtained wavelength and intensity of the spectral lines.

3.13 Energy-dispersive X-ray fluorescence (ED-XRF)
The atoms of the elements to be measured in the sample are subjected to high energy radiation and inner electron transition is induced to emit X-rays with certain energy levels. An X-ray detector with a given energy resolution is used to detect characteristic X-rays emitted by the element to be analysed in the sample, which is analysed qualitatively and quantitatively by the energy of the output signals of the detector.

3.14 Background
Continuous spectrum that overlies the analyte lines, caused principally by the scattering of the incident radiation by the sample

3.15 Analyte lines
Characteristic spectral lines, the intensity of which is measured to determine the content of the analysed element

3.16 Limit of detection
Minimum content that can be detected at a given confidence level

3.17 Interference lines
Spectral lines that overlay or partially overlay the analyte lines and therefore affect the accurate measurement of the intensity of analyte lines

3.18 Matrix effects
Effects of chemical or physical states of the sample on the intensity of analyte lines, principally manifested as absorption-enhancement effect, particle size effect, surface smoothness effect, and chemical state effect, etc

3.19 Gas chromatography-mass spectrometry (GC-MS)
A method in which a gas chromatograph and a mass spectrometer are connected to combine the high separation capacity of gas chromatography and feature identification of mass spectrometry to qualitatively and quantitatively analyse organic compounds.

3.20 Inductively coupled plasma atomic emission spectrometry (ICP-AES/OES)
Determining the target element contained in the sample by means of atomization and ionization of the sample with high-frequency plasma

3.21 Inductively coupled plasma mass spectrometry (ICP-MS)
Determining the target element contained in the sample by ionizing the sample with high-frequency plasma. The ions generated are measured by mass spectrometer for the number of ions and mass-to-charge ratio (m/z) of the target element or its isotopes.

3.22 Atomic Absorption Spectrometry (AAS)
Method of determining the chemical element content in a sample by converting the target element into free atoms through flame or chemical reaction, and measuring the characteristic electromagnetic absorption by the ground state atom of the element in vapour phase

3.23 Cold Vapour Generation Atomic Absorption Spectrometry (CVAAS)
Method of determining mercury content by reducing the mercury ions in the sample to free atoms and measuring the characteristic electromagnetic absorption by the ground state atom of the element in vapour phase

3.24 Atomic Fluorescence Spectrometry (AFS)
Method of qualitative and quantitative analysis by means of wavelength and intensity of atomic fluorescence spectral lines

4. Summary of testing methods

4.1 Contents of test methods
The test methods of hazardous substances and elements consist of the six parts below:

- Scope
- Apparatus and equipment
- Reagents
- Sample preparation
- Testing procedures

4.2 Flowchart of test methods

The sequence for standard testing procedure is illustrated in **Figure 1**, where the test unit is EIP-A/B/C as specified in SJ/T 11363-2006.

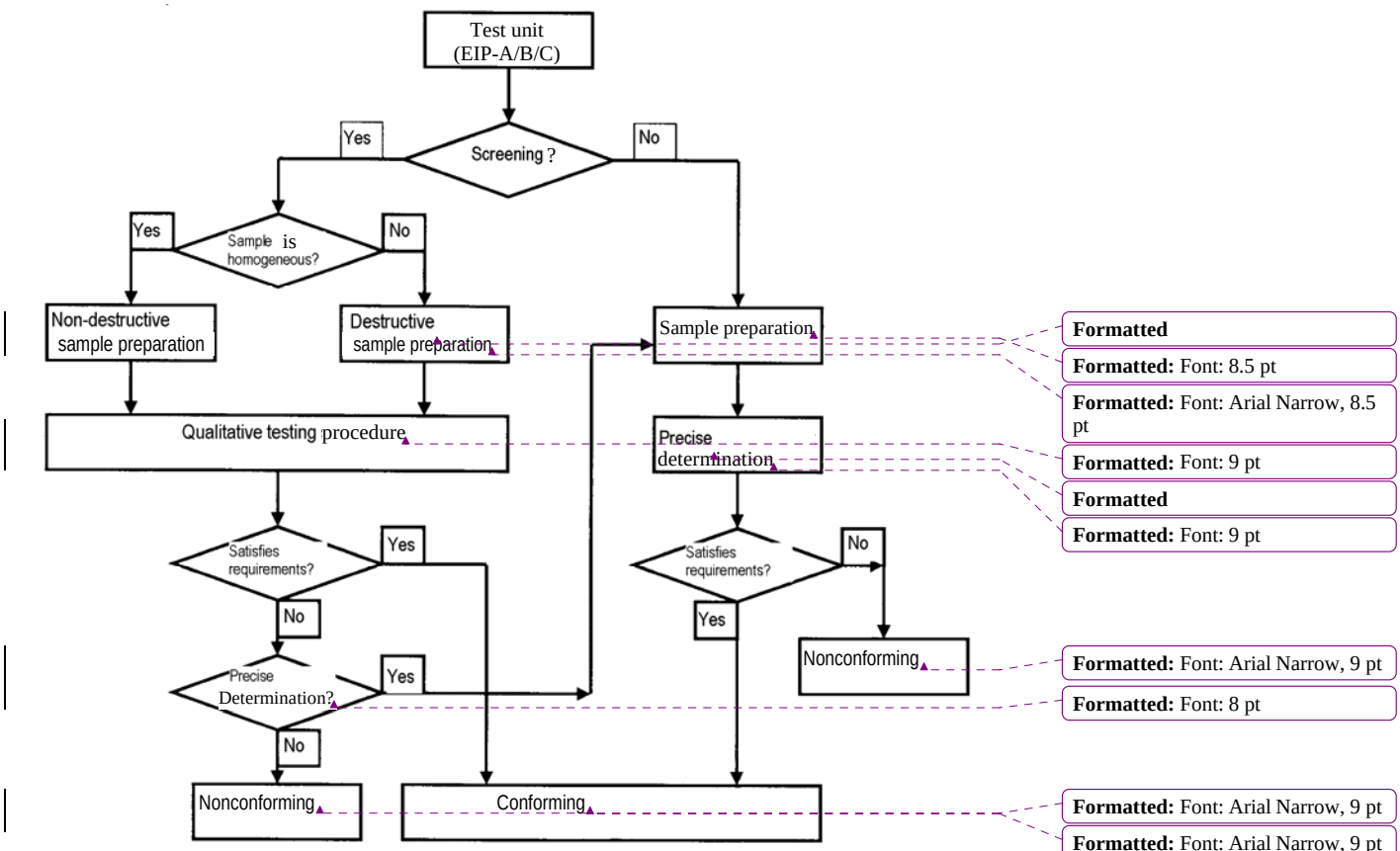


Figure 1 Flowchart of testing procedure

4.3 Screening test method

The target substances in the sample are tested using the energy-dispersive X-ray fluorescence (ED-XRF) and wavelength-dispersive X-ray fluorescence (WD-XRF) methods. The sample can be tested either directly (the sample remains intact), or after destruction of the sample to make it uniform (mechanical sample preparation). Screening of representative samples of many uniform materials (such as plastics, alloys, glass) can be done non-destructively, while for many complex samples (like printed circuit boards),

mechanical sample preparation is necessary. Mechanical sample preparation is applicable to both the screening and precise testing methods. The procedure for mechanical sample preparation is described in Annex A.

Note: Although the XRF spectroscopic method described in detail in Chapter 5 of this Standard is fast and resource-efficient way of analysis, there are limitations on the method and applicability of the results obtained.

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

- Pass (P): Concentrations of target substances are lower than the permissible values.
- Fail (F): Concentrations of target substances are higher than the permissible values.
- Inconclusive (X): Concentrations of target substances are around the permissible values, and additional investigations are required due to inconclusive analysis results

After screening, pass means conformity, fail means nonconformity, while inconclusive samples require precise determination procedures to verify conformity.

4.4 Precise testing method

The precise testing method employs multiple testing methods to analyse the concentrations of regulated materials in organic materials, metallic materials, inorganic non-metallic materials and special electronic materials. **Table 1** gives an overview of precise testing methods, which are described in detail in Chapters 6 to 8.

Table 1 Simplified overview of the precise measurement method

Step	Substance	Metallic materials	Polymer materials	Inorganic non-metallic materials	Special electronic materials
Mechanical sample preparation	-	Grinding	Grinding	Grinding	Grinding
Chemical sample preparation	-	Acid digestion	Microwave digestion Acid digestion Dry ashing Solvent extraction	Microwave digestion Acid digestion Solvent extraction	Microwave digestion Acid digestion Solvent extraction
Methods of analysis	PBB/ PBDE		Gas chromato-graphy – Mass spectrometry (see Chapter 6)		Gas chromato-graphy – Mass spectrometry (see Chapter 6)
	Pb/Cd	Inductively coupled plasma atomic emission spectrometry, Inductively coupled plasma mass spectrometry, Atomic absorption spectrometry (see 7.1)			
	Hg	Inductively coupled plasma atomic emission spectrometry, Inductively coupled plasma mass spectrometry, Cold vapour atomic absorption spectrometry, Atomic fluorescence spectrometry (see 7.1)			
	Cr (VI)	Coating colour development method (see 8.1), Alkaline digestion-Colorimetric method (see 8.2)	Alkaline digestion-Colorimetric method (see 8.2)	Alkaline digestion-Colorimetric method (see 8.2)	Alkaline digestion-Colorimetric method (see 8.2)

5. Testing method for screening for hazardous substances in electronic information products by X-ray fluorescence spectrometer

5.1 Scope

This Chapter specifies the screening testing methods for lead (Pb), cadmium (Cd), mercury (Hg), chromium (Cr) and bromine (Br) in electronic information products by X-ray fluorescence spectrometry.

This testing method is applicable to the testing of lead (Pb), cadmium (Cd), mercury (Hg), chromium (Cr) and bromine (Br) in various parts and materials after the mechanical sample preparation of electronic information products according to Annex A.

5.2 Summary of method

Samples of different materials prepared through the appropriate methods are placed inside the specimen chamber of the X-ray fluorescence spectrometer for X-ray analysis. According to the screening limitations of various elements in various samples, the contents of lead (Pb), cadmium (Cd), mercury (Hg), chromium (Cr) and bromine (Br) are evaluated for pass or fail, or if precise testing is necessary.

5.3 Apparatus and equipment

5.3.1 X-ray fluorescence spectrometer (wavelength dispersive X-ray fluorescence (WD-XRF) or energy dispersive X-ray fluorescence (ED-XRF) spectrometer: Consists principally of excitation source, detector, sample chamber and data processing system

5.3.2 Auxiliary equipment: Common auxiliary equipment includes automatic sampling device, sample cutting device, grinder, a pulverizer, homogenizer, sample press and oven, all of which must meet requirements as appropriate

5.3.3 Selection of parameters:

Element	Preferred analyte line	Second preferred analyte line	Organic sample analyte line	Metallic analyte line
Lead	Lβ	Lα	Lα	Lβ
Cadmium	Kα	-	Kβ	Kα
Mercury	Lα	-	Lα	Lα
Chromium	Kα	-	Kα	Kα
Bromine	Kα	Kβ	Kα	Kα

5.4 Reagents

5.4.1 Boracic acid (HBO_3): Analytical reagent, oven dried at 105° C for 1 hour and stored in a desiccator

5.4.2 Corresponding standard samples containing the five elements: lead, cadmium, mercury, chromium and bromine

5.4.2 Other reagents and materials used in the method shall be free of the tested elements and compounds of lead, cadmium, mercury, chromium and

bromine. Sample preparation shall not be subject to contamination from these elements or compounds.

5.5 Sample Preparation

5.5.1 Homogeneous block samples

Cutters and grinders may be used to machine unshaped test samples such as blocks, plates or castings, into samples with suitable dimensions for testing. The surface that is irradiated must be representative of the entire sample.

5.5.2 Film samples

Particular care shall be exercised to ensure the consistency and homogeneity of structure of the samples when preparing test samples from film samples. A backing material may be used to support the film in order to spread the film flat, while the background effect of the backing material shall be as low as possible.

5.5.3 Special electronic materials

Special electronic materials are generally not homogeneous. Samples may be cut with cutting equipment and cut into small pieces and then ground into powder with particle sizes of not more than 1 mm by a grinder. Mix the powder uniformly and then prepare samples in a press using boracic acid as supporting material. The thickness of the sample shall be not less than 1 mm.

5.5.4 Liquid samples

Liquids shall be divided into beakers volumetrically. Care shall be exercised in testing to avoid evaporation, leakage, bubbling, or precipitation. Liquid samples may also be dripped onto suitable carriers (e.g. filter paper) and dried before measurement.

5.5.5 Prevention of sample contamination

Contaminated samples cause analysis errors. In X-ray fluorescence spectrometry, particular care is required to prevent the contamination of the sample surface. During sample preparation, pay particular attention to the following aspects of contamination:

a) Contamination from the materials of the cutter or grinder
b) Contamination from the containers during dissolving and melting

c) Contamination from the working environment in the laboratory
d) Contamination by reagents
e) Contamination occurring when the hands touch the samples
f) Contamination from lining materials
g) Contamination occurring when samples are pressure moulded

5.6 Test procedures

5.6.1 Apparatus preparation

Install the instrument according to the manufacturer's instructions; the instrument shall operate continuously to maintain optimum consistency.

5.6.2 Preparation of standard curves

Place a group of samples with different known concentrations (no less than three concentrations) of each of the five elements, lead (Pb), cadmium (Cd), mercury (Hg), chromium (Cr) and bromine (Br), into the sample chamber. Carry out the test of the group of standard samples in the time recommended by the manufacturer, at least four times for each at each concentration, and take the average of the calculated results. Finally, prepare the standard curves according to the spectral line intensity and concentration of each element. The standard curves may be prepared automatically if a computerized analyser is available.

5.6.3 Calibration

Before each analysis of a sample, perform a calibration with a standard sample containing lead (Pb), cadmium (Cd), mercury (Hg), chromium (Cr) or bromine (Br) to check the validity of the standard curves.

5.6.4 Sample test

Place the properly prepared sample in the sample chamber, and perform X-ray analysis according to the selected testing mode. Test each sample at least twice and calculate the average of the test results.

5.6.5 Analysis of results

5.6.5.1 Calculation of results

Calculate the concentrations of each element in the samples from the spectral intensity of each element according to the testing mode selected.

5.6.5.2 Screening of elements

According to the screening limits of the elements in the samples in Table 2, the screening test results from X-ray fluorescence analysis of hazardous substances in electronic information products can be classified into three basic classifications:

- Pass (P): The analysis results of all elements are lower than the specified lower limits
- Fail (F): The analysis results of one of the tested elements are higher than the specified upper limits
- Inconclusive (X): The analysis results of all elements are between the specified upper and lower limits; precise tests are required

Table 2 Screening limits for different elements in different electronic information product samples

Elements	Polymer materials	Metallic materials	Inorganic non-metallic materials	Special electronic materials
Cadmium	P≤70<X<130F	P≤70<X<130F	P≤70<X<130F	P≤70<X<130F
Lead	P≤70<X<130F	P≤70<X<130F	P≤70<X<130F	P≤70<X<130F
Mercury	P≤70<X<130F	P≤70<X<130F	P≤70<X<130F	P≤70<X<130F
Bromine	P≤300<X	-	-	P≤250<X
Chromium	P≤700<X	P≤700<X	P≤700<X	P≤500<X

5.6.6 Applicability

Although X-ray fluorescence spectrometry is fast, non-destructive and inexpensive , full consideration shall be given in the test to the limitations and the applicability of the results obtained. It shall be particularly noted that if the result for Cr or Br is F, the presence of hazardous hexavalent chromium and polybrominated biphenyls and polybrominated diphenyl ethers cannot be proved; in contrast, if the test result is P, it can be concluded that the sample does not contain hexavalent chromium and polybrominated biphenyls and polybrominated diphenyl ethers. For samples containing heterogeneous

materials, such as samples of paints on the surface of plastics, both the effect of the film thickness on the sensitivity and the possibility of X-ray penetration down to substrates shall be considered. In addition, requirements for minimum testing areas and possible interference due to the smoothness of the sample surface shall also be considered. Interference resulting from the matrix background cannot be ignored.

5.6.7 Reporting of test results

Take the arithmetic average of the two test results and report it as the result in mass fraction (mg/kg).

6 Testing Methods for polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs) in electronic information products

6.1 Scope

This method is applicable to the determination of content of 100 mg/kg to 20,000 mg/Kg polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs) in polymer materials and special electronic materials from EIPs. Samples with lower concentrations can be tested if suitable concentrating and purifying steps are carried out.

6.2 Summary of method

In this method, polybrominated biphenyls and polybrominated diphenyl ethers are extracted from polymer materials and special electronic materials by Soxhlet extraction and are then tested by gas chromatography-mass spectrometry (GC-MS) in selected ion monitoring (SIM) mode to calculate their content in the polymer materials.

6.3 Apparatus and equipment

6.3.1 Equipment

a) Laboratory fume hood
b) Electronic analytical balance (precision 0.1 mg)
c) Glassware
d) Soxhlet apparatus with condenser
e) Heating device to fit the round flask for Soxhlet apparatus
f) Crushing device: include equipment such as cutter or scissors, grinder,

cryogenic grinding device, mainly for sample reduction
g) Furnace (400° C or higher)
h) Oven (capable of maintaining a constant temperature 105° C – 250° C)
i) 18# standard screen.

6.3.2 Equipment

a) Gas chromatography – temperature programmable with all necessary accessories such as injector (either manual or automatic) and capillary column
b) Capillary column: 10 m - 30 m (L) × 0.25 mm (ID) × 0.1 μm (film thickness), fused silica column (DB-5 or equivalent)
c) Mass spectrometer: Capable of generating 70 eV for analyte ionization. The scan range to cover 50m/z~1000.0m/z
d) Data analysis system: Capable of collecting, recording, storing, and processing MS data

6.4 Reagents

a) Solvents for extraction: acetone, toluene, cyclohexane, normal hexane, methanol, dichloromethane, isooctane and nonane
b) Standard stock solution (1000 mg/L): Can be either prepared using pure standard materials or purchased. The mixed standard isomer solution of common PBBs or PBDEs can also be purchased
c) Calibration standard: Prepare at least five calibration standard samples of various concentrations with the lowest concentration being slightly higher than the detection limit of this method. The four other concentration samples shall fall into the range of the actual samples.
d) Internal standard solution: Labelled $^{13}C_{12}$ BDEs or 4,4'-dibromoonctafluro biphenyl (f) or Penathrene D10 as recovery standard for the analysis of PBDEs. Labelled $^{13}C_{12}$ PBB or 4,4'-dibromooctafluoro biphenyl (f) or Penathrene D10 as recovery standard for the analysis of PBBs)
e) Liquid nitrogen: Industrial grade

6.5 Sample preparation

6.5.1 Sample reduction

Disassemble the electronic information products into material samples according to annex A. Cut the samples into pieces of 0.1 cm×0.1 cm using scissors or a cutter. After they have cooled, grind the samples to a size of no more than 1.0 mm in a mill (or equivalent) and then mix them well.

6.5.2 Extraction of Sample solution

Take 0.1 g - 0.2 g of the well mixed sample and measure its weight accurate to 0.0001 g. Transfer it into a cellulose mantle and place in the Soxhlet extractor. Add 50 ml-200 ml of toluene or other solvents (6.4 a) as well as the internal standard solution (6.4 d), followed by 1 - 2 grains of zeolite. Complete the Installation of the Soxhlet extractor and heat for 4 - 24 hours to extract. When the solution has cooled, transfer it to an appropriate volumetric flask and fill the flask with water to the mark. The solution may be used in tests directly. Dilute appropriately if the concentration of the determined substance in the sample is above the range of the concentration calibration curve.

6.6 Test procedure

6.6.1 Gas chromatography conditions

a) Injection port temperature: 250° C - 320°C
b) Initial temperature and holding time of column oven: 100° C, held for 1 – 3 min
c) Temperature programming conditions for column: Temperature programmed from 100° C - 320° C at 5° C - 20°C/min and constant for 5 min;
d) Carrier gas: Helium, flow rate: 1.2 ml/min
e) GC/MS interface temperature: 320° C
f) Injection mode: pulse injection
g) Sample size: 1 µl - 2 µl.

6.6.2 Mass spectrometry conditions

a) Ionization: EI
b) Electron energy: 70eV
c) Ion source temperature: 250-300°C; mass separator temperature: 150°C (recommended)
d) Resolution: Greater than 800 (preferably greater than 1000)
e) Analysis mode: Selected ion monitoring (SIM), ions monitored are shown in Table 3 and Table 4, respectively

6.6.3 Sample analysis

a) Power on the instrument and let it stabilize.
b) Calibrate the instrument using instrument calibration standards according to the requirements for the instrument.
c) Develop standard curves: Inject standard samples of various concentrations

(6.5 c) into GC/MS in turn. Develop the standard curves of the peak vs concentration of the standards.
d) Sample determination: Inject sample extracts of the same size in standard curves developing into GC/MS, and determine the PBBs and PBDEs according to the ion peaks given in Table 3 and Table 4. Calculate the corresponding PBB and PBDE contents on standard curves by the peaks.

Table 3 Molecular weight and identification ion peaks of polybrominated biphenyls

Number	Chemical name	Molecular formula	Molecular weight	Quantitative ion	Identification ion peaks		
1	Mono-BBs	$C_{12}H_9Br$	233.1	234.0	236.0	232.0	152.2
2	Di-BBs	$C_{12}H_8Br_2$	312.0	312.0	314.0	310.0	152.2
3	Tri-BBs	$C_{12}H_7Br_3$	390.9	391.8	393.8	389.8	230.0
4	Tetra-BBs	$C_{12}H_6Br_4$	469.8	469.8	467.8	309.9	307.9
5	Penta-BBs	$C_{12}H_5Br_5$	548.7	549.6	547.6	389.8	387.8
6	Hexa-BBs	$C_{12}H_4Br_6$	627.6	627.6	625.5	467.7	465.7
7	Hepta-BBs	$C_{12}H_3Br_7$	706.5	705.5	703.5	545.5	543.6
8	Octa-BBs	$C_{12}H_2Br_8$	785.4	785.4	783.4	625.5	627.5
9	Nona-BBs	$C_{12}HBr_9$	864.3	703.4	863.2	705.4	703.4
10	Deca-BBs	$C_{12}Br_{10}$	943.2	781.3	943.2	783.3	781.3

Table 4 Molecular weight and Identification ion peaks of polybrominated diphenyl ethers

Number	Chemical name	Molecular formula	Molecular weight	Quantitative ion	Identification ion peaks		
1	Mono-BDEs	$C_{12}H_9BrO$	249.1	250.0	252.0	248.0	141.0
2	Di-BDEs	$C_{12}H_8Br_2O$	328.0	328.0	330.0	325.9	168.0
3	Tri-BDEs	$C_{12}H_7Br_3O$	406.9	405.8	403.8	246.0	123.0
4	Tetra-BDEs	$C_{12}H_6Br_4O$	485.8	485.7	483.7	325.9	162.9
5	Penta-BDEs	$C_{12}H_5Br_5O$	564.7	564.6	562.6	403.8	201.9
6	Hexa-BDEs	$C_{12}H_4Br_6O$	643.6	483.7	643.5	483.7	241.9
7	Hepta-BDEs	$C_{12}H_3Br_7O$	722.5	561.6	721.5	561.6	563.6
8	Octa-BDEs	$C_{12}H_2Br_8O$	801.4	641.5	801.4	641.5	320.8
9	Nona-BDEs	$C_{12}HBr_9O$	880.3	719.4	881.3	719.4	360.7
10	Deca-BDEs	$C_{12}Br_{10}O$	959.2	799.3	959.2	799.3	400.3

6.6.4 Calculation of results

Polybrominated Biphenyls (PBBs) and Polybrominated Diphenyl Ethers (PBDEs) contents in the sample are calculated from the equation:

$$X_i = \frac{C_i \times V_i \times d}{m_i} \times 10^6 \qquad (1) \qquad (3)$$

Where:

X_i — PBB and PDBE i contents in the sample in ppm (mg/kg);

C_i - PBB and PDBE i contents in the sample extracts in mg/L;

V_i - Volumetric size of n the sample extracts in L;

d - Dilution rate of the sample extracts;

m_i - Sample size in mg

6.6.5 Precision

The absolute deviation of two results from duplicate testing shall not exceed 20% of the arithmetic average.

7 Testing Methods for Lead (Pb), Cadmium (Cd) and Mercury (Hg) in Electronic Information Products

7.1 Testing methods for lead (Pb) and cadmium (Cd) in electronic information products

7.1.1 Scope

This method is applicable to the determination of Lead (Pb) and Cadmium (Cd) content in polymer materials, metal materials, special electronic materials and inorganic non-metallic materials.

7.1.2 Summary of method

An appropriate mass of sample is treated by microwave digestion, acid digestion, or dry ashing to prepare a homogenous liquid. The concentrations of lead (Pb) and cadmium (Cd) in the digestion solution are determined by inductively coupled plasma-atomic emission spectrometer (ICP - AES), inductively coupled plasma-mass spectrometer (ICP-MS) or atomic absorption spectrometer (AAS).

7.1.3 Apparatus and equipment

a) Atomic absorption spectrometer (AAS)
b) Inductively coupled plasma-atomic emission spectrometer (ICP-AES/OES)
c) Inductively coupled plasma-mass spectrometer (ICP-MS)
d) Laboratory glassware
e) Heater
f) Muffle furnace
g) Microwave digestion system equipped with polytetrafluoroethylene - tetrafluoroethylene high pressure digestion vessel
h) Electronic analytical balance capable of accurate weighing to 0.1mg
i) Crucibles, 50ml or 150ml
j) Hydrofluoric acid resistant holder
k) Bunsen burner, or similar type of gas burner

7.1.4 Reagents

Unless otherwise stated, only approved high purity reagents and 18 MΩ deionized water or equivalent purity water shall be used.

a) Nitric acid: ρ = approx. 1.4g/ml, 65%
b) Hydrochloric acid: ρ = approx. 1.16g/ml, 37%
c) Hydrogen peroxide: ρ = approx. 1.10g/ml, 30%
d) Sulphuric acid: ρ = approx. 1.84g/ml, 95%
e) Hydrofluoric acid: ρ = approx. ISO 40 ≈ 42%; JIS 46 ≈ 48%
f) Hydrobromic acid: ρ = approx. 1.48 g/ml, 47 ~ 49%
g) Perchloric acid: ρ = approx. 1.67 g/ml, 70%
h) Phosphoric acid: ρ = approx .1.69 g/ml, above 85%
i) Boracic acid
j) Mixed acid 1 (hydrochloric acid: nitric acid, 3:1)
k) Mixed acid 2 (hydrochloric acid: hydrogen peroxide, 3:1)
l) Mixed acid 3 (nitric acid: hydrofluoric acid, 1:3)
m) Mixed acid 4 (hydrofluoric acid: 1nitric acid, 2:2)
n) Lead standard solution, 1000 μg/ml
o) Cadmium standard solution, 1000 μg/ml
p) Scandium standard solution, 1000 μg/ml
q) Yttrium standard solution, 1000 μg/ml
r) Rhodium standard solution, 1000 μg/ml

7.1.5 Sample preparation

7.1.7.1 Sample reduction

Disassemble the electronic information products into the various material samples according to Annex A. Cut the samples into pieces 10 mm × 10 mm × 10 mm using shears or a cutting device (or in other manner). Metal materials and inorganic non-metallic materials can be used directly in the next step, while polymer materials and special electronic materials must be pulverized into particles or powder not more than 1mm in diameter and mixed uniformly for the next step.

7.1.5.2 Preparation of metal material sample

7.1.5.2.1 Acid digestion method

Take about 0.1 g to 0.2 g of sample into a beaker and measure its weight accurately to 0.0001 g. Add an appropriate amount of acid (or suitable proportion of mixed acid) according to the metal material matrix, and heat the beaker and its contents until the sample is dissolved completely. Hydrochloric acid, nitric acid or mixed solutions [7.1.4.1 (m)] are recommended. Use hydrofluoric acid, perchloric acid or sulphuric acid for further dissolution if the sample is found indigestible. A PTFE/PFA beaker is required if hydrofluoric acid is used.

Note: There may be some precipitate (lead sulphate, barium sulphate, silver chloride, alumina or aluminium hydroxide etc.) during sample dissolution. Therefore, the selected dissolution method shall not result in the loss of the target element. Another method is required for sample digestion (for example, alkali fusion or sealed pressure vessel) if target substances are included in the residues.

a) General alloy method

Place about 0.1 g - 0.5 g (weight can be adjusted according to the content of the tested elements) of sample in a beaker and measure its weight accurate to 0.0001 g. Slowly add 10 ml of mixed acid 1 of hydrochloric acid and nitric acid (adjusted according to the composition of matrix materials). Heat the beaker and its contents at low temperature until the sample dissolves completely. Gradually cool the solution to room temperature and transfer the contents to a 50 ml volumetric flask. Then fill the flask with water to the mark. Dilute the sample to the required concentration according to the method used.

It is necessary to add another 1 ml of hydrofluoric acid in order to ensure complete digestion of the sample when the sample contains Si, Zr, Hf, Ti, Ta, Nb or W. (See Chapter 5)

b) Tin alloy method

Place about 0.1 g - 0.5 g (can be adjusted according to the content of the tested elements) of sample in a beaker and measure its weight accurate to 0.0001 g. Slowly add 10 ml of mixed acid 1 of hydrochloric acid and nitric acid (can be adjusted according to the composition of matrix materials). Cover the beaker with watch glass to allow the reaction to be finish, and heat the beaker gently until the sample is dissolved completely. Allow the beaker to cooled for a while and remove the watch glass. Add 10 ml of sulphuric acid along the beaker wall and heat the beaker until white fumes of SO_3 are generated. Allow the sample to cool. Add 20 ml of hydrobromic acid along the beaker wall and mix the contents well. Then heat the beaker until white fumes of SO_3 are generated. Repeat these steps three times. Allow the beaker and its contents to cool to room temperature. Add 10 ml of nitric acid to dissolve salts. After cooling, transfer the solution to a 50 ml volumetric flask and then fill the flask with water to 50 ml. Dilute the sample to the desired concentration according to the method used.

Alternatively, take about 0.5 g of sample and measure its weight accurate to 0.0001 g, and add 10ml of mixed acid 2 hydrochloric acid and hydrogen peroxide (can be adjusted according to the composition of matrix materials) to dissolve the sample.

It is necessary to add another 1 ml of hydrofluoric acid in order to ensure complete digestion of the sample when the sample contains Si, Zr, Hf, Ti, Ta, Nb or W. (See Chapter 5)

7.1.5.2.2 Microwave digestion (mainly for insoluble alloys)

Weigh about 0.10 g of sample accurate to 0.0001 g. Transfer it into a digestion vessel, and add 5 ml of mixed acid 1 of hydrochloric acid and nitric acid in appropriate proportions (can be adjusted according to the composition of matrix materials). It is necessary to add another 1ml of concentrated hydrofluoric acid in order to ensure complete digestion when the sample contains Si, Zr, Hf, Ti, Ta, Nb or W. (See Chapter 5)

After a period of reaction of the sample, put the whole vessel in a microwave

digestion device. Digest the sample according to the operating instructions until it is dissolved completely. Take out the digestion vessel, and after the vessel has cooled to room temperature, add a suitable amount of boric acid to permit the complexing of the excess hydrofluoric acid (boracic acid is not required if a hydrofluoric acid resistant atomizer is used). Transfer the solution to a 50 ml volumetric flask and fill the flask with water to 50 ml. Dilute the sample to the desired concentration according to the method used.

7.1.5.3 Preparation of inorganic non-metallic materials

Hydrofluoric acid resistant vessels must be used, because some non-metallic elements such as silicon are typically contained in inorganic non-metallic samples and extremely corrosive hydrofluoric acid is required during the preparation of samples.

Weigh 0.10 g of sample accurate to 0.0001 g. Transfer it into a digestion vessel, and add 3 ml of mixed acid 1 of concentrated hydrochloric acid and concentrated nitric acid in appropriate proportions and 3 ml of concentrated hydrofluoric acid. After a period of reaction of the sample, place the whole vessel in a microwave digestion device. Digest the sample according to the operating instructions until it is dissolved completely. Take out the digestion vessel, and after the vessel has cooled to room temperature, add a suitable amount of boric acid to permit the complexing of the excess hydrofluoric acid (boracic acid is not required if a hydrofluoric acid resistant atomizer is used). Transfer the solution to a 50 ml volumetric flask and fill the flask with water to 50 ml. Dilute the sample to the desired concentration according to the method used.

7.1.5.4 Preparation of polymer material sample

7.1.5.4.1 Dry ash method

a) If the sample does not contain halogen compounds (See Chapter 5)

Place 0.1 g - 0.5 g (weight can be adjusted according to the content of the tested elements) of crushed sample in a beaker and weigh accurately to 0.0001 g. Mount the crucible in the hole in the heat resistant thermal insulation board and then heat it gently. 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. Then transfer the crucible and its contents 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. Then remove the crucible and its contents from the furnace and allow it to cool to ambient temperature. Add 5 ml of nitric acid, and transfer the resulting solution to a 50 ml volumetric flask and fill the flask with water to 50 ml. Dilute the sample to the desired concentration according to the method used.

b) When the sample contains halogen compounds (See Chapter 5)

Place 0.1 g - 0.5 g (weight can be adjusted according to the content of the tested elements) of crushed sample in a crucible and weigh accurately to 0.0001 g. Add 10 ml to 15 ml of sulphuric acid and heat the crucible and its contents slowly on a hot plate or sand bath until the plastic melts and blackens. Then add 5 ml of nitric acid and continue heating until the plastic degrades completely and white fumes are generated. After cooling, place the crucible in a muffle furnace maintained at 450° ± 25° C and evaporate, dry, and burn until the carbon has been completely incinerated. Then remove the crucible and its contents from the furnace and allow them to cool to room temperature. Add 5 ml of nitric acid, and transfer the resulting solution to a 50 ml volumetric flask and fill the flask with water to 50 ml. Dilute the sample to the desired concentration according to the method used.

7.1.5.4.2 Acid digestion method

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

a) General dissolution method

Place 0.1 g - 0.5 g (weight can be adjusted according to the content of the tested elements) of crushed sample in a flask and weigh accurately to 0.0001 g. Add 5 ml of sulphuric acid and 1 ml of nitric acid, and heat the flask and until the sample is reduced to ash and white fumes are generated. Stop heating and add nitric acid in small quantities (approx. 0.5 ml), and resume heating until white fumes are generated. Repeat heating and decomposition with nitric acid until the decomposed solution turns pale yellow.

Then allow the sample to cool for several minutes. Add hydrogen peroxide in small quantities, several milliliters at a time, and heat the sample once again until white fumes are generated. After cooling, transfer the solution to a 50 ml volumetric flask and fill the flask with water to the mark. Dilute the sample to the desired concentration according to the method used.

b) If general digestion is inadequate or when the sample contains silica, titanium, etc (See Chapter 5)

Place 0.1 g - 0.5 g (weight can be adjusted according to the content of the tested elements) of crushed sample in a flask and weigh to 0.0001 g. Add 5 ml of sulphuric acid and 1 ml nitric of acid, and heat until the sample is reduced to ash and white fumes are generated. Stop heating, add nitric acid in small quantities (approx. 0.5 ml) and resume heating until white fumes are generated. Repeat the heating and decomposition with nitric acid until the decomposed solution turns pale yellow.

Then allow the sample to cool for several minutes. Add hydrogen peroxide in small quantities, several milliliters at a time, and heat the sample once again until white fumes are generated. After cooling, transfer the solution to a fluorocarbon resin vessel. Add 5 ml of hydrofluoric acid and heat the vessel until white fumes are generated. Then remove the digestion vessel and its contents from the furnace and allow to cool to ambient temperature. Add the proper amount of boric acid to permit the complexing of excess hydrofluoric acid (boracic acid is not required if a hydrofluoric acid resistant atomizer is used). Transfer the solution to a 50 ml volumetric flask and fill the flask with water to 50 ml. Dilute the sample to the desired concentration according to the method used.

7.1.5.4.3 Microwave digestion

Weigh 0.10 g of crushed sample accurate to 0.0001 g. Transfer it into a digestion vessel, and add 5 ml of nitric acid and 1 ml of hydrogen peroxide. Add another 1 ml of concentrate hydrofluoric acid if the sample contains Si, Zr, Hf, Ti, Ta, Nb or W. (See Chapter 5). Put the whole vessel in a microwave digestion device. Digest the sample according to the operating instructions until it is dissolved completely. Take out the digestion vessel, and after the vessel has cooled to room temperature, add the appropriate amount of boric acid to permit the complexing of the excess hydrofluoric acid (boracic acid is not required if a hydrofluoric acid resistant atomizer is used). Transfer the solution to a 50 ml volumetric flask and fill the flask with water to 50 ml. Dilute the sample to the desired concentration according to the method used.

Note: Hydrogen peroxide may react rapidly and violently on easily oxidizable materials and should not be added if the sample might contain large quantities of easily oxidizable organic constituents.

7.1.5.5 Preparation of special electronic materials sample

Weigh 0.10 g of crushed sample accurate to 0.0001 g. Transfer it into a digestion vessel, and add 5 ml of mixed acid 1 of hydrochloric acid and nitric acid in appropriate proportions (can be adjusted according to the composition of matrix materials). Add another 1 ml of concentrated hydrofluoric acid if the sample contains Si, Zr, Hf, Ti, Ta, Nb or W. (See Chapter 5).

After a period of reaction, put the whole vessel in a microwave digestion device. Digest the sample according to the operating instructions until it is dissolved completely. Take out the digestion vessel, and after the vessel has cooled to room temperature, add an appropriate amount of boric acid to permit the complexing of excess hydrofluoric acid (boracic acid is not required if a hydrofluoric acid resistant atomizer is used). Transfer the solution to a 50 ml volumetric flask and fill the flask with water to 50 ml. Dilute the sample to the desired concentration according to the method used.

7.1.6 Test procedure

7.1.6.1 Preparation of blank solution

Execute procedure identical to the preparation of the test sample solution in 7.1.5 concurrently without sample to prepare a blank solution.

7.1.6.2 Preparation of calibration solution of lead and cadmium

Because of the different extent of matrix effects in different analysers, the standard solution preparation method shall be selected from calibration method (matrix matching method), internal standard method, and standard-addition method according to the test materials.

Prepare a calibration blank and at least three calibration standards as calibration solutions.

If the internal standard method is employed, an internal standard element may be added in the solution either in preparation or added inline by apparatus during testing. For ICP-AES/OES, scandium and yttrium can be selected as internal standard elements; for ICP-MS, rhodium can be used as an internal standard element. The concentration of the internal standard element is equivalent to that of the tested element.

7.1.6.3 Preparation of calibration curves of lead and cadmium

a) ICP-AES/OES method

Determine the readings for the emission intensity of the target elements (and, if required, that of the internal standard element) of calibration solution series from low to high concentration.

In the calibration curve method, the curve showing the relationship between the emission intensity of the target elements and their concentration is plotted as the calibration curve.

In the internal standard method, the curve showing the relation between intensity against concentration of the target elements with respect to that of the internal standard elements is plotted as the calibration curve.

Selected spectral lines and potential interferences in the analysis are shown in **Table 5**.

Table 5 Spectra of cadmium and lead and potential interference

Interference element	Spectral line (nm)							
	Cd	Cd	Cd	Cd	Pb	Pb	Pb	Pb
	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					+	+	+	+

+ +	No or small interference (Strength of interference by 1000 mg/kg matrix elements is typically no more than 0.05ppm)
+ +	Medium interference (Strength of interference by 1000 mg/kg matrix elements is about 0.05 ppm - 0.2ppm)
+ +	Strong interference (Strength of interference by 1000 mg/kg matrix elements is above 0.2ppm)

In the case of interference from co-present substances, either select a wavelength that does not interfere with the calibration range or adopt a suitable means of eliminating the interference.

b) ICP/MS method

Determine the isotope count of the target elements (and, if required, that of the internal standard element) of calibration solution series from low to high concentration.

In the calibration curve method, the curve showing the relationship between the emission intensity of the target elements and their concentration is plotted as the calibration curve.

In the internal standard method, the curve showing the relation between intensity against concentration of the target elements with respect to that of the internal standard elements is plotted as the calibration curve.

Selected isotope and potential interferences in the analysis are shown in **Table 6**.

Table 6 Isotopes of cadmium and lead and potential interferences

Element	Isotope	Potential isotope interference	Potential molecule and ion interference
Cd	111	/	MoO, MoOH, ZrOH
	112	Sn	MoO, MoOH
	113	In	MoO, MoOH, ZrOH, RuO
	114	Sn	MoO, MoOH, RuO
Pb	204	/	/
	206	/	PtO
	207	/	IrO
	208	/	PtO

In the case of interference from co-present substances, either select an isotope that does not interfere with the calibration range or make adjustments in interference volume using a suitable method.

c) AAS method

Determine the readings for the emission intensity of the target elements of the calibration solution series from low to high concentration.

Analytical line: Cadmium (Cd) 228.8nm, lead (Pb) 217.0nm or 283.3nm
Absorbance reading range: The absorbance readings typically vary between 0.1 and 0.6. If necessary, adjust the concentration of solution and the length of light path, or extend the measurement range.

In the case of interference from co-present substances, either select a wavelength that does not interfere with the calibration range or make adjustments in interference volume using a suitable method.

7.1.6.3 Sample analysis

After the calibration curve is plotted, measure the calibration blank, sample solution and spike samples solution. The corresponding concentration is available from the calibration curve based on the signal reading of each sample. Every sample should be determined twice and the relative standard deviation should be no more than 10% and the recovery of spike samples should be between 90% and 110%.

For AAS, if the sample concentration is above the range of the concentration curve, the solution shall be diluted to the range of the calibration standards.

Use standard substances or calibration solutions as quality control samples and check measurement precision with them (such as once every ten samples). If necessary, plot calibration curves again.

7.1.6.4 Calculation of analytical results

The content of tested element in %, which is represented by mass fraction W_M, is calculated from the equation:

$$W_M = \frac{(C_1 - C_2) \times V \times d \times 10^{-6}}{m} \times 100 \qquad (2)$$

Where:
C_1: Value of tested element concentration of sample solution read from the calibration curve, in μg/ml
C_2: Value of tested element concentration of blank solution read from the calibration curve, in μg/ml
V: Volume of the solution, in ml
d: Dilution rate of the sample solution
m: Sample size, in g

Take the arithmetic average of the two testing results and report it as the result in mass fraction (mg/kg).

7.1.6.6 Precision

The absolute deviation of two results from duplicate testing shall not exceed 10% of the arithmetic average.

7.2 Testing methods for mercury (Hg) in electronic information products

7.2.1 Scope

This method is applicable to the determination of mercury (Hg) content in polymer materials, metal materials, special electronic materials and inorganic non-metallic materials.

7.2.2 Summary of method

An appropriate mass of sample is treated by microwave digestion, acid digestion, or dry ashing to prepare homogenous liquid. The sample solution should be stored at 4 °C to minimize evaporation. For longer term storage of mercury, it is recommended to use a 5.0% nitric acid + 0.05% potassium permanganate solution.

The element mercury in the obtained digestion solution is determined by cold vapour atomic absorption spectrometry (CVAAS), atomic fluorescence spectrometry (AFS), inductively coupled plasma-atomic emission spectrometer (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) or atomic absorption spectrometry (AAS) . When using CV-AAS and AFS, the mercury is reduced to the elemental state before it is analysed.

7.2.3 Apparatus and equipment

a) Cold vapour atomic absorption spectrometer (CVAAS)

b) Inductively coupled plasma mass spectrometer (ICP-AES/OES)
c) Inductively coupled plasma mass spectrometer (ICP-MS)
d) Atomic fluorescence spectrometer (AFS)
e) Heating and reflux device equipped with reaction flask, reflex condenser and absorption vessel
f) Laboratory glassware
g) Hydrofluoric acid resistant sample holder
h) Heating device
i) Microwave digestion system with Polytetrafluoroethylene - tetrafluoroethylene high pressure digestion vessel
j) Electronic analytical balance capable of accurate weighing to 0.1mg

Note: Because of the sensitivity of the described mercury analytical techniques, each sampling step should be performed with great care. All sampling, storage and manipulation devices must be mercury-free. Soak all glassware in 50 % (m/m) nitric acid for 24 hours at room temperature, and then rinse thoroughly with grade 1 water, specified in ISO 3696:1987.

7.2.4 Reagents

Unless otherwise stated, only approved high purity reagents and 18 MΩ deionized water or equivalent purity water shall be used.

a) Nitric acid: ρ = approx. 1.40 g/ml, 65%
b) Hydrochloric acid: ρ = approx. 1.19 g/ml, 37;
c) Hydrogen peroxide: ρ = approx. 1.10 g/ml, 30%
d) Hydrofluoric acid: ρ = approx. ISO 40% ≈ 42%; JIS 46% ≈ 48%
e) Sulphuric acid: ρ = approx. 1.84 g/ml, 95%
f) Boracic acid (HBO_3)
g) Mercury standard solution, with concentration of 1000 μg/ml
h) Sodium chloride - hydrochloric acid hydroxylamine solution: 12 g sodium chloride and 12g hydrochloric acid hydroxylamine dissolved in 100 ml water
i) Potassium permanganate (G.R.): 5% aqueous solution (w/v); dissolve 5 g of potassium permanganate in 100 ml of distilled water
j) Sodium hydroxide
k) Sodium tetrahydridoborate
l) Potassium borohydride (trace metal grade), sodium hydroxide, G.R. 1 % in 0.05 % NaOH: Add approximately 1000 ml of distilled water to a 1L volumetric flask followed by the addition of 0.05 g sodium hydroxide. Add 10.0 g potassium borohydride and stir to dissolve. Dilute it to scale with

distilled water. The solution shall be prepared on site.
m) BCR 680, BCR-681: Certified reference materials in plastics packaging and packaging materials

7.2.5 Sample preparation

7.2.5.1 Sample reduction

Disassemble the electronic information products into material samples according to Annex A. Cut the samples into pieces 10 mm × 10 mm ×10 mm using a shear or cutting machine (or in other manner). Metal materials and inorganic non-metallic materials can be used directly in the next step, while polymer materials and special electronic materials must be pulverized into particles or powder not more than 1 mm in diameter and mixed uniformly for the next step.

7.2.5.2 Preparation of metal material sample

7.2.5.2.1 Acid digestion method

a) General preparation method of samples

Place about 1 g of sample in a clean reaction flask and weigh accurately to 0.0001 g. Then add 30 ml conc. HNO_3. The flask is furnished with a reflux condenser and an absorption vessel containing 10 ml 0.5 Mol/L HNO_3, before the temperature program is started to digest the samples for 1 h at room temperature. Raise the temperature to 90 °C and digest under constant temperature for 2 hours. After cooling to room temperature, put the content of the absorption tube into the reaction vessel and transfer the resulting solution into a 250 ml volumetric flask and fill the flask with 5 % (m/m) HNO_3 to the mark.

b) Digestion of materials containing zirconium (Zr), hafnium (Hf), titanium (Ti), copper (Cu), silver (Ag), tantalum (Ta), niobium (Nb) or tungsten (W)

Place about 1 g of sample in a clean reaction flask and add 20 ml of concentrated hydrochloric acid and 10ml of concentrated nitric acid. The flask is furnished with a reflux condenser and an absorption vessel containing 10 ml 0.5 Mol/L HNO_3, before the temperature program is started to digest the samples for 1 h at room temperature. Raise the temperature to 95 °C ± 5°C and digest under constant temperature for 15 minutes. Remove the sample from the heating digester and let it cool 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 distilled water and 15 ml of $KMnO_4$ solution to the reaction chamber. Mix thoroughly and continue heating for 30 min at 95° C ± 5° C. After cooling to room temperature the solution is quantitatively transferred over a filter into a 100 ml volumetric flask. Rinse the reaction chamber, condenser and absorber tube with the distilled water, and transfer the rinse solution into the volumetric flask. Add 6 ml of sodium chloridehydroxylamine-hydrochloride to reduce the excess permanganate. Dilute the digested sample solution to the mark with distilled water and mix thoroughly.

7.2.5.2.2 Microwave digestion

Take about 0.10 g of sample and weigh accurately to 0.0001 g. Transfer it into a digestion vessel, and add 5 ml of mixed acid solution of hydrochloric acid and nitric acid in appropriate proportions (a typical ratio of hydrochloric acid and nitric acid is 3:1, according to the composition of matrix materials). Add another 1 ml of concentrated hydrofluoric acid if the sample contains Si, Zr, Hf, Ti, Ta, Nb or W. (See Chapter 5)

After a period of reaction, put the whole vessel in a microwave digestion device. Digest the sample according to the operating instructions until it is dissolved completely. Take out the digestion vessel, and after the vessel is cooled to room temperature, add an appropriate amount of boric acid to permit the complexing of excess hydrofluoric acid (boracic acid is not required if a hydrofluoric acid resistant atomizer is used). Transfer the solution to a 50 ml volumetric flask and fill the flask with water to 50 ml. Dilute the sample to the desired concentration according to the method used.

7.2.5.3 Preparation of inorganic non-metallic material

Hydrofluoric acid resistant vessels must be used, because some non-metallic elements such as silicon are typically contained in inorganic non-metallic samples and extremely corrosive hydrofluoric acid is required during the preparation of samples.

Weigh 0.10 g of sample accurate to 0.0001 g. Transfer it into a digestion vessel,

and add 3 ml of mixed acid solution of concentrated hydrochloric acid and concentrated nitric acid in appropriate proportions (a typical ratio of hydrochloric acid and nitric acid is 3: 1, according to the composition of matrix materials) and 3 ml of concentrated hydrofluoric acid. After a period of reaction, place the whole vessel in a microwave digestion device. Digest the sample according to the operating instructions until it is dissolved completely. Take out the digestion vessel, and after the vessel has cooled to room temperature, add an appropriate amount of boric acid to permit the complexing of excess hydrofluoric acid (boracic acid is not required if a hydrofluoric acid resistant atomizer is used). Transfer the solution to a 50 ml volumetric flask and fill the flask up with water to 50 ml. Dilute the sample to the desired concentration according to the method used.

7.2.5.4 Preparation of polymer materials sample

Weigh 0.10 g of sample accurate to 0.0001 g. Transfer it into a digestion vessel, and add 5 ml of nitric acid and 1 ml of hydrogen peroxide. Add another 1 ml of concentrated hydrofluoric acid if the sample contains Si, Zr, Hf, Ti, Ta, Nb or W. (See Chapter 5.) Put the whole vessel in a microwave digestion device. Digest the sample according to the operating instructions until it is dissolved completely. Take out the digestion vessel, and after the vessel has cooled to room temperature, add an appropriate amount of boric acid to permit the complexing of excess hydrofluoric acid (boracic acid is not required if a hydrofluoric acid resistant atomizer is used). Transfer the solution to a 50 ml volumetric flask and fill the flask with water to 50 ml. Dilute the sample to the desired concentration according to the method used.

Note: Hydrogen peroxide may react rapidly and violently on easily oxidizable materials and should not be added if the sample may contain large quantities of easily oxidizable organic constituents.

7.2.5.5 Preparation of special electronic materials samples

Weigh 0.10 g of sample accurate to 0.0001 g. Transfer it into a digestion vessel, and add 5 ml of mixed acid solution of concentrated hydrochloric acid and concentrated nitric acid in appropriate proportions (a typical ratio of hydrochloric acid and nitric acid is 3: 1, according to the composition of matrix materials). Add another 1 ml of concentrated hydrofluoric acid if the sample contains Si, Zr, Hf, Ti, Ta, Nb or W. (See Chapter 5.) After a period of reaction, put the whole vessel in a microwave digestion device. Digest the sample according to the operating instructions until it is dissolved completely. Take out the digestion vessel, and after the vessel has cooled to room

temperature, add an appropriate amount of boric acid to permit the complexing of excess hydrofluoric acid (boracic acid is not required if a hydrofluoric acid resistant atomizer is used). Transfer the solution to a 50 ml volumetric flask and fill the flask with water to 50 ml. Dilute the sample to the desired concentration according to the method used.

7.2.6 Test procedure

7.2.6.1 Preparation of calibration solution of mercury

The standard mercury solution shall be stored in an inert plastic container. The stable period of mercury solutions with concentrations of 1000 μg/ml is more than 1 year, and solutions with concentrations lower than 1 μg/L shall be prepared on site.

The stability of mercury standard solutions can be severely affected because mercury tends to be absorbed to the internal walls of the container. Therefore it is recommended to stabilize mercury standard solutions by the addition of a few drops of 5 % $KMnO_4$ solution.

Because of the different extent of matrix effects in different analysers, a method of standard solution preparation shall be selected from the calibration method (matrix matching method), internal standard method, and standard-addition method according to the tested materials.

Prepare a calibration blank and at least three calibration standards as calibration solutions.

When the internal standard method is employed, the internal standard element may be added in the solution either in preparation or added inline by apparatus during testing. For ICP-AES, scandium and yttrium can be selected as internal standard elements; for ICP-MS, rhodium can be used as an internal standard element. The concentration of the internal standard element is equivalent to that of tested element.

7.2.6.3 Preparation of calibration curve of mercury

a) ICP-AES/OES method

Determine the readings for the emission intensity of mercury (and that of the internal standard element as appropriate) of the calibration solution series from low to high concentration.

In the calibration curve method, the curve showing the relationship between the emission intensity of mercury and its concentration is plotted as the calibration curve.

In the internal standard method, the curve showing the relation between intensity against concentration of mercury with respect to that of the internal standard elements is plotted as calibration curve.

Selected spectral line of mercury in the analysis: 194.227 nm

b) ICP/MS method

Determine the isotope count of mercury (and, if required, that of the internal standard element) in the calibration solution series from low to high concentration.

In the calibration curve method, the curve showing the relationship between the emission intensity and the concentration is plotted as the calibration curve.

In the internal standard method, the curve showing the relation between intensity against concentration of mercury with respect to that of the internal standard elements is plotted as the calibration curve.

Isotope of mercury selected for analysis in calibration curve method and internal standard method: m/z = 202

c) CVAAS method

Determine the readings for the emission intensity of mercury in the calibration solution series from low to high concentration, and plot the curve showing the relationship between the emission intensity of mercury and its concentration as the calibration curve.

Absorbance reading range: The absorbance reading typically varies between 0.1 to 0.6 to minimize the error of absorbance measurement. If necessary, adjust the concentration of the solution and the length of light path, or extent of the measurement range
Light source: Hg electrode-less discharge lamp or hollow cathode lamp
Wavelength: 253.7 nm
Slit width: 0.7 nm
Purge gas: N_2 or Ar

Reduction agent: 3% $NaBH_4$ (dissolved in 1% NaOH)

d) AFS method

Determine the readings for the fluorescence intensity of mercury in the calibration solution series from low to high concentration.

The curve showing the relationship between the fluorescence intensity of mercury and its concentration is plotted as the calibration curve.

Fluorescence intensity reading range: the fluorescence intensity readings shall fall into the linear range of the instrument to minimize the error of absorbance measurement. If necessary, adjust the concentration of the solution.

Instrument parameters:
Light source: Hg hollow cathode lamp, current: 30 mA,
Wavelength: 253.7 nm
Minus high-voltage: 360 V
Furnace temperature: 800° C
Argon flow Carrier gas: 600 ml/min, Screen gas: 1000 ml/min
Reducing agent: 3% $NaBH_4$ (dissolved in 1% NaOH)

7.2.6.4 Sample analysis

After the calibration curve is plotted, measure the calibration blank and sample solution. The corresponding concentration is available from calibration curve based on the signal reading of each sample. Every sample should be determined twice and the relative standard deviation should be no more than 20% and the recovery rate of samples should be between 70% and 130%.

For AAS, if the sample concentration is above the range of the concentration curve, the solution shall be diluted to the range of the calibration standards.

The effect of matrix composition on the redox reaction shall be taken into account when CVAAS or AFS is selected.

The standard substance or calibration solution shall be used as a quality control sample and the measurement precision shall be checked against it (such as once every ten samples). If necessary, calibration curves shall be plotted again.

7.2.6.5 Calculation of analytical results

The content of tested elements in %, which is represented by mass fraction W_M, is calculated from the equation:

$$W_M = \frac{(C_1 - C_2) \times V \times d \times 10^{-6}}{m} \times 100 \quad \cdots\cdots (3)$$

where:
C_1: Value of tested element concentration in sample solution read from the calibration curve; μg/ml
C_2: Value of tested element concentration of blank solution read from the calibration curve; μg/ml
V: Volume of solution; ml
d：Dilution rate of sample solution
m: Sample size; g

7.2.6.6 Prevention of mercury contamination

Cautious handling of apparatus and careful technique will minimize this problem. The following precautions contribute to avoiding sample contamination:

a) Only use distilled or deionized water. Care must be taken that all materials in contact with the water are composed of 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 shall be used.

c) Always 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 recommended that inert plastics be used for sample handling.

e) For measurements by ICP-AES (-OES) and ICP-MS and AFS, the memory effect occurs in cases where high concentrations of mercury are introduced. Therefore when the tested solution has a high concentration of mercury, a

sampling system with a memory effect as low as possible shall be selected, or the sample solution shall be diluted, and the sampling system shall be fully cleaned after the measurement.

7.2.6.7 Precision

The absolute deviation of two results from duplicate testing shall not exceed 20% of the arithmetic average.

8. Determination of hexavalent chromium in electronic information products by colorimetric method

8.1 Qualitative testing of hexavalent chromium

8.1.1 Scope

This method is applicable to the qualitative determination of hexavalent chromium in metal coatings.

8.1.2 Summary of method

Clean the surface of the sample with detergent, soft cloth or a suitable solvent and drip diphenylcarbazide colorimetric solution. Observe the colour change in the following several minutes to qualitatively determine the presence of hexavalent chromium.

8.1.3 Apparatus and equipment

None

8.1.4 Reagents

All reagents shall be A.R. grade

a) Diphenylcarbazide
b) Acetone
c) Alcohol (95%)
d) Orthophosphoric acid solution (75%)
e) Deionized water

8.1.5 Sample preparation

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

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

8.1.6 Test procedure

Dissolve 0.4 g of 1,5-diphenylcarbazide in a mixture of 20 ml acetone and 20 ml ethanol (95%) and 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). Drip 1 to 5 drops of the test solution prepared above on the treated sample surface. A red to violet colour appearing within a few minutes indicates that hexavalent chromium is present in the solution in a concentration above 1 mg/kg. The following quantitative method can be used directly for metals with surface colouring, since there is interference with the qualitative method.

8.2 Determination of hexavalent chromium by colorimetric method

8.2.1 Scope

This method is applicable to the quantitative test for hexavalent chromium in metal materials, polymer materials, inorganic non-metallic materials and special electronic materials in electronic information products.

8.2.2 Summary of method

Treat the sample by a suitable method according to the type of material, and extract hexavalent chromium from the sample with an alkaline extraction solution. Adjust the pH of the resulting solution and add diphenylcarbazide under acidic conditions. Determine the concentration in the solution by a colorimetric apparatus after 5 - 10 minutes for complete colour development.

The sample and its extract shall be stored at 4 °C to reduce the chemical activity of hexavalent chromium. Because the stability of hexavalent chromium in the extract cannot be determined, analysis shall be performed as quickly as possible. Solutions and wastes containing Cr (VI) shall be disposed of properly, e.g. Cr (VI) can be reduced to Cr (III) with ascorbic acid or other reducing agents.

8.2.3 Apparatus and equipment

a) Vacuum filtration apparatus
b) Heating and stirring devices
c) pH gauge: To read pH range 0 - 14 with accuracy ± 0.03 pH units
d) Analytical balance: with an accuracy of 0.1 mg
e) Thermometer or thermistor or other temperature measurement device: Capable of measuring up to 100° C
f) Colorimetric equipment: Either a spectrophotometer, for use at 540 nm, providing a light path of 1 cm or longer, or a filter photometer, providing a light path of 1 cm or longer and equipped with a green-yellow filter having maximum transmittance near 540 nm
g) Laboratory glassware
h) Hot plate

8.2.4 Reagents

Unless otherwise stated, only approved high purity reagents and 18 MΩ deionized water or equivalent purity water shall be used.

a) Nitric acid: Analytical reagent grade. Store at 20° C - 25° C away from light. Do not use concentrated HNO_3 if it has a yellow tinge; this is indicative of photoreduction of NO_3^- to NO_2, a reducing agent for Cr(VI).
b) Sodium carbonate: Anhydrous, analytical reagent grade
c) Sodium hydroxide: Analytical reagent grade
d) Magnesium chloride: Anhydrous, analytical reagent grade. A mass of 400 mg $MgCl_2$ is approximately equivalent to 100 mg Mg^{2+}
e) Phosphate buffer (pH 7.0): Dissolve 87.09 g K_2HPO_4 (analytical reagent) and 68.04g KH_2PO_4 (analytical reagent) in 700 l of distilled water. Transfer to a 1L volumetric flask and dilute to volume.
f) Lead chromate: Analytical reagent grade.
g) Digestion solution: Dissolve 20.0 ± 0.05 g NaOH and 30.0 ± 0.05 g Na_2CO_3 in distilled water in a 1L volumetric flask and dilute to the mark. Store the solution in a tightly capped polyethylene bottle and prepare fresh monthly. The pH of the digestion solution must be 11.5 or greater before using; discard

the solution if it is not.
h) Potassium dichromate stock solution: Dissolve 141.4mg of dry potassium dichromate, $K_2Cr_2O_7$ (analytical reagent grade), in distilled water and dilute to 1L (5 µg/ml of Cr (VI)).
i) Potassium dichromate standard solution: Dilute 10 ml of the potassium dichromate stock solution to 100 ml (5 µg/ml of Cr (VI)).
j) Sulphuric acid, 10% (v/v): Dilute 10 ml of distilled reagent grade sulphuric acid, H_2SO_4, to 100 ml with water.
k) 1,5-Diphenylcarbazide: Analytical reagent grade
l) Potassium dichromate tagged stock solution (1000 mg/l Cr (VI)): Dissolve 2.829 g of dry (105°C) $K_2Cr_2O_7$ in distilled water in a 1L volumetric flask and dilute to the mark. Alternatively, a 1000 mg/l Cr (VI) certified primary standard solution can be used. Store in a refrigerator for use up to six months.
m) Potassium dichromate, $K_2Cr_2O_7$, matrix tagging solution (100 mg/l Cr (VI)): Add 10.0 ml of the 1000 mg Cr (VI)/l $K_2Cr_2O_7$ tagging stock solution made above to a 100 ml volumetric flask and dilute to volume with distilled water. Mix well.
n) Acetone: analytical reagent grade.
8.2.5 Sample preparation

Disassemble the electronic information products into the various material samples according to Annex A. Cut the samples into pieces 10 mm × 10 mm × 10 mm. Collect the samples and place them in containers that do not contain stainless steel. Grind the samples into a fine powder capable of passing through a #500 screen (i.e. brass or stainless steel #35) with a grinder after liquid nitrogen cooling and mix well.

8.2.5.1.2 Preparation of metal coating samples

Prior to the test, the sample surface shall be free of all contaminants, fingerprints and other extraneous stains. Remove any surface thin oil prior to the test using a clean, soft lab wipe wetted with a suitable solvent, or by rinsing the surface with a suitable solvent at room temperature (not exceeding 35° C). The samples shall not be subject to forced drying at temperatures in excess of 35° C. Alkaline solutions shall not be used as chromate coatings are broken down by alkalis. If there is a polymer coating over a sample surface, a gentle abrasion with a fine sandpaper, such as a SiC grinding paper with 800 grit size, may be applied to remove the polymer layer, but without removing the chromate coatings on the sample.

8.2.5.2 Extraction of hexavalent chromium

8.2.5.2.1 Extraction of hexavalent chromium from metal materials, polymer materials, inorganic non-metallic materials and special electronic materials

a) Prepare colour developing solution: Dissolve 250 mg 1,5-diphenylcarbazide (analytical reagent) in 50 ml acetone. Transfer the solution into a brown bottle and store it in a refrigerator. Discard if the solution becomes discoloured.
b) Take about 5 g of sample and measure its weight accurately to 0.1 mg. Place the sample into a clean Erlenmeyer flask. Alternative sample amounts may also be used for samples with potentially very low or very high Cr (VI) concentrations.
c) To each sample, add 50 ml ±1 ml of digestion solution (8.2.4 g)) measured with a graduated cylinder. Also add approximately 400 mg of $MgCl_2$ (8.2.4 d) and 0.5 ml of phosphate buffer (8.2.4 e) to each sample. For polymer samples that appear to float on the surface of the digestion solution, add one to two drops of a wetting agent (e.g. *Triton X-100*) at this time to increase the sample wetting during digestion. Cover the Erlenmeyer flask with a watch glass.
d) Stir while heating the samples continuously to 90° C - 95° C, then maintain the samples at 90° C - 95° C for at least 3 h with constant stirring.
e) Gradually cool, each solution to room temperature with continued agitation. Transfer the contents quantitatively to the filtration apparatus, rinsing the digestion vessel with three successive portions of distilled water. Transfer the rinse solutions to the filtration apparatus. Filter through a 0.45μm membrane filter. Rinse the inside of the filter flask and filter pad with distilled water and transfer the filtrate and the rinse solution to a clean 250ml vessel.
f) With constant stirring, slowly drip concentrated nitric acid solution [8.2.4 a)] into the 250ml vessel. Adjust the pH of the solution to 7.5 ± 0.5. Remove the stirring device and rinse, collecting the rinse solution 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 distilled water. Mix well.
g)Transfer the extract to be tested volumetrically to a clean 100 ml beaker and add water to make the volume of the solution near 95 ml. Add 2.0 ml diphenylcarbazide solution [8.2.5.2.1 a)] and mix. Slowly add H_2SO_4 solution to the beaker and adjust the pH of the solution to 2 ± 0.5. Transfer quantitatively the contents of the beaker to a 100 ml volumetric flask and adjust the sample volume to 100 ml with distilled water. Let stand 5 to 10 minutes for full colour development.

8.2.6 Test procedure

8.2.6.1 Preparation of standard 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 in measured volumes into a 10 ml volumetric flask to generate standard concentrations ranging from 0.1 mg/l to 5 mg/l Cr (VI) when diluted to the appropriate volume. An alternative concentration range of the calibration curve should be used if the Cr (VI) concentration in the sample solution is outside the original calibration curve.
c) Develop the colour of the standards as for the samples.
d) Transfer an appropriate portion of the standard solution to a 1 cm absorption cell and measure its absorbance at 540 nm in a colorimeter.
e) Correct the absorbance reading of the sample by subtracting the absorbance of a blank carried through the colour development procedures.
f) Construct a calibration curve by plotting the corrected absorbance values against μg/ml of Cr (VI).

8.2.6.2 Sample test

a) Transfer an appropriate portion of the solution to a 1 cm absorption cell and measure its absorbance at 540 nm with a colorimeter.
b) Correct the absorbance reading of the sample by subtracting the absorbance of a blank carried through the colour development procedures.
c) From the corrected absorbance, determine the mg/l of Cr (VI) present by reference to the calibration curve.

8.2.6.3 Calculation of analytical results

a) Cr (VI) concentration in total sample:

$$C = \frac{A \times D \times F}{S} \quad \cdots\cdots (4)$$

where
C: Cr (VI) concentration (mg/kg)
A: Concentration observed in the digest (μg/ml)
D: Dilution factor
F: Final digest volume (ml)
S: Initial sample mass (g)

b) Cr (VI) concentration in metal coating

$$C = \frac{A \times D \times F}{L} \quad \cdots\cdots (5)$$

where
C: Cr (VI) concentration (mg/kg)
A: Concentration observed in the digest (μg/ml)
D: Dilution factor
F: Final digest volume (ml)
S: Initial mass of coating in sample (g)
Note: Coatings on samples can be removed by diluted aqua regia solution or other acid solution, i.e. by acid stripping. Dip the sample into such acid solutions for a moment and take it out, check its surface 1 min later for change, to find whether the surface coating has been etched. The weight of the coating can be obtained by measuring the sample mass before and after acid stripping.
c) Cr (VI) concentration in metal coating

$$C = \frac{A \times F}{S} \quad \cdots\cdots (6)$$

where
C: Cr (VI) concentration (μg/cm^2)
A: Concentration observed in the digest (μg/ml)
F: Final digest volume (ml)
S: Surface area of sample (cm^2)
d) Error (RPD)

$$RPD = \{|(S-D)| / [(S+D)/2]\} \times 100\% \quad \cdots\cdots (7)$$

Where
S : Initial sample result (μg)
D: Duplicate sample result (μg)
e) Spike recovery

$$SPR = \frac{SSR - SR}{SA} \times 100\% \quad \cdots\cdots (8)$$

where :
SPR - Spike recovery (μg)
SSR - Spike sample result (μg)
SR - Untagged sample result (μg)
SA - Spike added (μg)

8.2.6.4 Quality Control

At least one separately prepared duplicate sample must be analyzed at a frequency of one per batch (20 samples or fewer). Duplicate samples must have a relative percentage difference of not more than 20%.
A sample shall be analyzed as a spike sample per batch (20 samples or fewer). Soluble matrix spike samples are tagged with 1.0 ml of the matrix tagging solution (8.2.4 m) or at twice the sample concentration, whichever is greater. The insoluble matrix spike is prepared by adding 1 mg – 2 mg of $PbCrO_4$ (8.2.4 f) to a sample or at twice the sample concentration, whichever is greater. The matrix tagged sample is then carried through the digestion process and colorimetric measurement procedures and the recovery is calculated from equation 8.2.6.3 e. The acceptance range for matrix spike recovery is 75-125%, otherwise the sample batch should be reanalyzed.

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

The entire surface area shall be selected for metallic parts, and if the surface area is too large, it can be sealed with paraffin or other heat resistant organic compounds. The sample for investigation shall be subjected to mechanical pretreatment before extraction. In order to fulfill the minimum requirements for correct analysis, the maximum grain size and minimum amounts of sample are given in the standard. It is highly likely that after the digestion, solid residues will be present. Different analytical means should be used to ensure that no target elements are included in these residues. Alternatively they should be resolved by different chemical approaches and be combined with the test sample solution. This standard strongly recommends the use of sophisticated equipment for digestion. Nevertheless, if the user is certain of the suitability of a simpler approach, it may be applied. Any deviation from the described procedures shall be evaluated and documented in the test report.

Annex A
(Normative)
Method of sample preparation in hazardous substances test

A1 Structure of electronic information products

A1.1 Construction

A1.1.1 Complete machine: Such as a television set, telephone or computer

A1.1.2 Part: A structural unit that can be disassembled by means of simple tools, such as a circuit board, power supply, module and screw.

A1.1.3 Essential electronic component: A structural electronic component of a circuit board, such as a resistor, capacitor, integrated circuit, lighting part or detachable plug board.

A1.1.4 Raw materials: Basic structural materials of an essential electronic component or structural part, such as metals, plastics, solders, adhesives, paintings or cleaners.

A1.2 Connection method classification

A1.2.1 Physical connection: Methods of joining or fixing two different materials by means of physical force such as pressure, friction or gravity. Common examples include: crimping, riveting, bonding, binding, screwing, locking, covering and looping.

A1.2.2 Chemical connection: Method of joining two different materials through metallurgical or chemical reactions to form the connection. Common examples include welding, electroplating, chemical plating and bonding.

A1.3 Risk areas and forms of hazardous substances

A1.3.1 Lead: Plastic additives, pigments, stabilizers, batteries, solders, cladding, glass, light bulbs, solid lubricants, rubbers, etc

A1.3.2 Cadmium: Plastic additives, coatings in electrical contacts, batteries, springs, joints, PCBs, fuse wire, pigments and paintings, semiconductor photoelectric sensors, etc

A1.3.3 Mercury: Plastic additives, colorants, fluorescent lamps, thermostats, sensors, relays, metal etching agents, batteries, rust preventive agents, disinfectants and adhesives, etc

A1.3.4 Hexavalent chromium: Anti-rust coatings on metals, pigments, rust preventive agents, corrosion preventive agents and ceramics, etc

A1.3.5 PBBs and PBDEs: Fireproofing agents for organic materials, PCBs, joints and plastic housing, etc

A2 Purpose and principles of electronic information products disassembly

A2.1 Purpose

In order to accurately measure the concentrations of hazardous substances in electronic information products and to provide effective controls over the use of toxic substances in electronic information products, the products shall be disassembled into the basic structural parts and units prior to test. (See **Table A.1** for details.)

Table A.1 Purpose of disassembly electronic information products (EIPs)

Structural unit	Definition of basic structural unit or materials
EIP-A	Homogenous substances of electronic information products
EIP-B	Coating material of parts in electronic information products
EIP-C	Small parts in electronic information products, i.e. small or non-homogeneous parts that cannot be further disassembled and are 4 mm^3 or less in volume

A2.2 Principles of disassembly

A2.2.1 Electronic information products must be disassembled strictly in accordance with the purposes for disassembly listed in Table A.1, and after they have been disassembled, all structural elements must be assigned to category A, B or C.

A2.2.2 In order to balance the operability and efficiency of the tests, an assessment of the risk of hazardous substances shall be carried out according to A.1.3 prior to disassembly. If the risk of toxic substances is very low (adventitious additions at low levels and possibility of contamination by toxic substances in the production process is also relatively low), the part does not

need further disassembly.

A2.2.3 Separation of any special materials or special members from other parts (EIP – A/B/C) shall be considered first in sample preparation.

A2.2.4 Chemical joints that are coatings (EIP-B) can be tested with XRF or SEM/EDS directly for qualitative or semi-quantitative determination; for multilayer coatings, cross-sections can be prepared for testing to determine whether the regulated substances were added deliberately when the coating was made. The sample preparation of bulk (substrate) materials shall be performed by removing the coated layer by mechanical or chemical means. For terminal connections between similar or different materials, the connection shall be disconnected and the non-chemical parts are to be taken for sample preparation.

A2.2.5 If these technical means are not sufficient to disassemble an electronic information product and to prepare a sample, consideration may be given to substituting measurements of a sample of structural materials with measurements from the same batch of materials.

A3 Typical examples of disassembly

A3.1 When disassembling a circuit board (as in Figure A.1), select the largest solder points possible and take the solder material in them; avoid taking coating layers of wiring and pads. At the same time, take care to select the adhesives that are used for joints or fixtures in disassembling electronic units and parts.

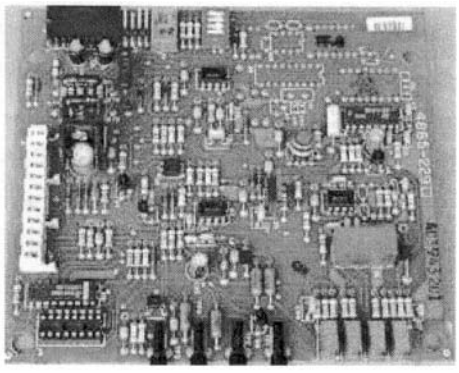
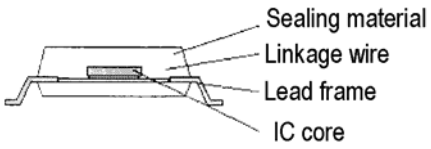


Figure A.1 Typical electronic circuit board

A3.2 Example of disassembly of electronic integrated circuits with pins

There are many types and shapes of integrated circuits with pins, including DIP, SOP and QFP, with QFP being the most typical. This example is of the disassembly of a QFP type integrated circuit.

QFP

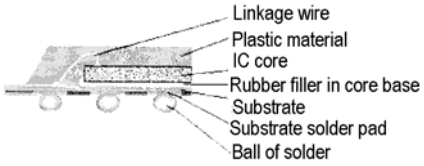


The principal risk with QFP type integrated circuits is that there may be lead in the leads and other hazardous substances in plastic packages. The main body of the integrated circuit may also contain high temperature lead solders, which are a form of special material. Integrated circuits >4 mm^3 in bulk shall be disassembled into two parts: the pins and the rest of the body. QFP type integrated circuits <1.2 mm^3 need not be disassembled. They should be treated as EIP-C as provided for in A2.2.

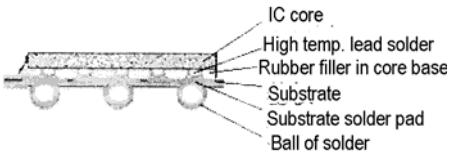
A3.3 Example of disassembly of array type integrated circuits

More specifically, array type integrated circuits include the ball grid array and column grid array, and they may consist of one or multiple types of array. Some examples of ball grid arrays are PBGA, FCBGA, CSP and WLCSP etc. The principal risks with BGA and CSP type integrated circuits is the lead in the solder globules, and other hazardous substances that may be present in the plastic package material. The main body of these integrated circuits often contains special types of materials (exempt materials) such as high temperature solder containing lead.

Examples of disassembly of PBGA and FCBGA type integrated circuits are shown in Figure A.3.



PBGA



FC-BGA

Criterion: It is possible to separate the solder and main body

A3.4 Example of disassembly of printed circuit boards

Printed circuit boards may be classified into inorganic substrates and organic substrates according to the properties of the substrate materials. They generally consist of silk screen printing inks, solder block films, solder pads, surface layer copper wires, inner layer copper wires, porous plated copper and the substrate. The important points to be considered with this type of circuit board are the coated layer of the pad and ink patterns, as well as the additives and flame-retardants that may be found in the organic materials.

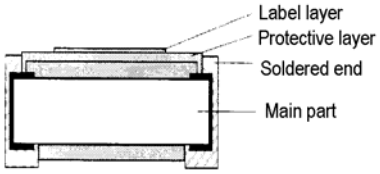
Method of disassembly: The solder pad, printing ink and the organic material need to be cut for sample preparation.

Test the solder pad as for a category EIP-B coated layer.

Cut a sample from a position on the organic substrate that does not contain any parts, perforations or copper.

A3.5 Example of disassembly of rectangular tabular part without pins

There are many different types and shapes of rectangular tabular parts without pins. This example is of the disassembly of a particular type of resistor as shown in Figure A.4.



A tabular shaped resistor consists of a label layer, a protective layer, solder ends and the main part.

Criteria for disassembly:

If volume is $\leq$1.2 mm^3, use the whole unit as the sample
If volume is >1.2 mm^3: if the solder forms a plated layer, prepare a sample in the normal manner for plated layers; if there is a physical join, disassemble the terminals and sample
Sample material of the main part directly.

A3.6 Example of disassembly of separate plug-in units

There are many types of such units, including resistors, capacitors, sensors and diodes and triodes.

Criteria for disassembly:

Sample with leads sheared:

If the volume is $\leq$ 1.2 mm^3, use the whole unit as the sample
If the volume is >1.2 mm^3, refer to the general principles on disassembly to sample

A3.7 Example of disassembly plug-in electrolytic capacitors

The structures of plug-in electrolytic capacitors are relatively complex; they consist principally of a casing, rubber, electrolyte solution, electrolyte paper separators, aluminium foil, aluminium casing and pins.

If the volume of the main part of the capacitor is $\leq$1.2 mm^3, disassemble into the pins and main part.
If the volume of the main part of the capacitor is >1.2 mm^3, disassemble into the pins, outer casing, separator and positive and negative poles.

A3.8 Example of disassembly of wires and cables

There are very many types of wires and cables, such as electrical wire, electrical cable, optical fibres and optical cable.

These types of materials have relatively simple structures, generally consisting of an outer protective layer, an inner protective layer and an inorganic core. They should be disassembled according to their structures.

A3.9 Metal coating samples

Prepare samples according to the principles listed in A2.2, or carry out determination with qualitative methods such as XRF or colorimetry without sample preparation.

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10. ISO 17294-1 Water quality - Application of inductively coupled plasma mass spectrometry (ICP-MS) - Part 1: General guidelines
11. ISO 3613:2000(E) Chromate Conversion Coatings on Zinc, Cadmium, Aluminium-Zinc alloys, and Zinc-Aluminium alloys - Test method
12. IEC 111/54/CDV Procedures for the determination of levels of six regulated substances (Lead, Mercury, Cadmium, Hexavalent Chromium, Polybrominated Biphenyls, Polybrominated Diphenyl Ethers) in electronic products
13. EPA 3540C Soxhlet Extraction
14. EPA 3050 Acid Digestion of Sediments, Sludges and Soils
15. EPA 3052 Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices
16. EPA 7000 Series Method for determining Pb, Cd, Cr and Hg
17. EPA 7471A, Mercury in Solids using CVAAS (Manual)
18. EPA 7470A, Mercury in Water using CVAAS (Manual)
19. EPA 7474, Mercury in sediment and tissue by AFS
20. EPA 3060A Alkaline Digestion for Hexavalent Chromium,1996.12
21. EPA 7196A Chromium, Hexavalent (Colorimetric),1992.7
22. ASTM D3421 Recommended Practice for Extraction and Determination of Plasticizer Mixtures from Vinyl Chloride Plastics