

Sharp's RoHS analysis method guideline [Ver.2.2]

I. General

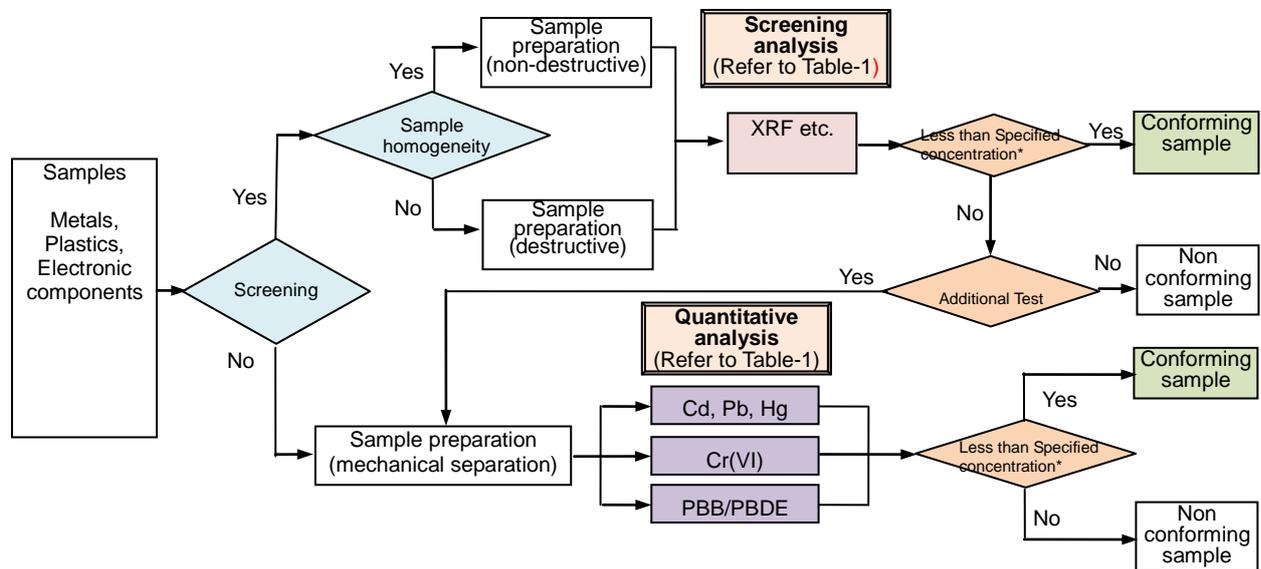
(1) How to proceed RoHS analysis

The basic way of RoHS analysis is shown in Fig.1 in the form of a flowchart. Conformance shall be determined either by screening analysis by means of an X-ray fluorescence spectrometer (XRF) etc.* shown in Table-1 or by quantitative analysis by means of ICP-OES or other methods also shown in Table-1. If the result of screening analysis turns out to be in the gray zone shown in Table-2 or Table-3, additional quantitative analysis shall be carried out for a final determination. If no additional test is carried out even though the result of analysis is in the gray zone, such a test sample shall be taken as a nonconforming item.

If any other analysis method than shown in Table-1 is to be used, documents that support the reliability of such analysis method shall be submitted to contact address shown at the end of this document.

However, if a certain analysis method is specified by the Device Group's suppliers, use of such an analysis method shall not be inhibited.

*: Including 2nd screening for PBB and PBDE by Pyro/GC-MS etc., after 1st screening by XRF.



*: Specified concentration : Cd 100ppm, Pb (Resin) 300ppm, Others 1000ppm.
Heavy metal contained in packaging material 100ppm (Based on the total amount of all heavy metals)

Figure-1 Flow chart of the methods(In conformity to IEC62321 [Ed1])

(2)Applied analytical method

Table-1. Overview of the analysis method [Ver.2.2](In conformity to IEC62321 [Ed1])

Steps	Substances	Plastics	Metals, Ceramics	Electronic components
Sample preparation	Mechanical sample preparation (homogenized) (see IEC62321 Clause 5)	Direct measurement, Cutting, milling or grinding	Direct measurement, Cutting, milling or grinding	Cutting, milling, Grinding
	Chemical sample preparation	Microwave digestion, Acid digestion, Dry-ashing, Solvent extraction	Microwave digestion, Acid digestion	Microwave digestion, Acid digestion, Solvent extraction
Screening/Qualitative Analysis	5 elements (Hg, Pb, Cd, Br, Cr)	X-ray fluorescence (XRF) (see IEC62321 Clause 6)		
	PBBs ,PBDEs ^(*)	IAMS, HPLC-UV, Pyro/GC-MS		IAMS, HPLC-UV, Pyro/GC-MS
Analytical technique definition (Definition of abbreviations are described last page.)	Hg	CV-AAS, CV-AFS, ICP-OES, ICP-MS(see IEC62321 Clause 7)		
	Pb/Cd	ICP-OES, ICP-MS, AAS (see IEC62321 Clause 8)	ICP-OES, ICP-MS, AAS (see IEC62321 Clause 9)	ICP-OES, ICP-MS, AAS (see IEC62321 Clause 10)
	PBB/PBDE	GC-MS (see IEC62321 Annex A)	NA	GC-MS (see IEC62321 Annex A)
	Cr(VI)	Alkaline digestion / colorimetric method (see IEC62321 Annex C)	Boiling water extraction procedure(see IEC62321 Annex B) ^{(*)2}	Alkaline digestion / colorimetric method (see IEC62321 Annex C)

*1: Regarding PBB/PBDE, IAMS, HPLC-UV and Pyro/GS-MS can be used for 2nd screening, after 1st screening by XRF.

*2: Hot water (80°C) extraction/color development method is available. Determination of conformance with spot test method is not accepted.

II. Qualitative/quantitative analysis

(1) Screening/qualitative analysis by X-ray fluorescence (XRF)

When a test sample is subjected to screening measurement using X-ray fluorescence and the reading is $N \pm 3\sigma$ [unit: ppm], the value of 3σ is substituted in the judgment formula in Table-2. And if the value of N is BL, the test sample is judged as being conforming, if the value is OL, it is judged as being nonconforming, and if the value is X, it is judged as being in the gray zone.

The judgment formula in Table-2 serves as a basis for judgment, but the accurate analysis more than formula in Table-2 is possible depending on analysis organizations, analysis equipment, test samples, measurement conditions, etc. When it is appropriate to narrow the gray zone, a special exception for the judgment formula is approved. In this case, an application for approval shall be submitted to contact address shown at the end of this document, together with documents that support the accuracy.

When a plated test sample is subjected to screening by X-ray fluorescence, use of a thin film FP method is essential.

Table-2. Screening limits in mg/kg for regulated elements in various matrix
(extract from IEC62321 Ed1 Annex D)

Element	Plastics	Metals	Electronic components
Cd	$BL \leq (70 - 3\sigma) < X < (130 + 3\sigma) \leq OL$		$LOD < X < (150 + 3\sigma) \leq OL$
Pb	$BL \leq (700 - 3\sigma) < X < (1300 + 3\sigma) \leq OL$		$BL \leq (500 - 3\sigma) < X < (1500 + 3\sigma) \leq OL$
Hg			
Br	$BL \leq (300 - 3\sigma) < X$	—	$BL \leq (250 - 3\sigma) < X$
Cr	$BL \leq (700 - 3\sigma) < X$		$BL \leq (500 - 3\sigma) < X$

X: region where further investigation is necessary, BL: Below Limit, OL: Over Limit, LOD: Limit of detection
X-ray fluorescence cannot identify PBB, PBDE, Cr(VI), therefore you cannot judge OL(over limit) about Br and Cr.

(2) 2nd Screening/qualitative analysis for PBBs and PBDEs

The existence of PBBs and PBDEs cannot be judged by Screening by XRF. When the value of Br in a test sample by using XRF is in the gray zone, IAMS, HPLC-UV or Pyro/GC-MS can be used for 2nd screening. After measuring the value of Br by using these equipment, the measured value N[unit: ppm] is substituted in the judgment formula in Table-3. If N is in BL, it is judged as a conforming sample. If not, it is judged as a sample in the gray zone. The sample in the gray zone has to be judged whether it is confirming sample or not by using quantitative analysis.

Additionally, the judgment formula of Table-3 will basically be used in most cases. However, according to the analysis organization, analysis equipment, test samples and measurement conditions etc., the analysis that is more accurate than formula in Table-3 may be able to be used. Therefore, if it is possible to narrow the gray zone, a special exception for the judgment formula is approved. In this case, related documents for approval has to be submitted to contact address (head office) shown at the end of this document.

Table-3. Judgment formula for 2nd Screening limits of PBBs and PBDEs

	Plastics	Metals	Electronic components
PBBs, PBDEs	$BL \leq 500 < X$	—	$BL \leq 500 < X$

X: Gray zone for judgment, BL: Below Limit

Judgment value of gray zone (500ppm) for PBBs and PBDEs are in conformity to draft of IEC62321 [Ed2]

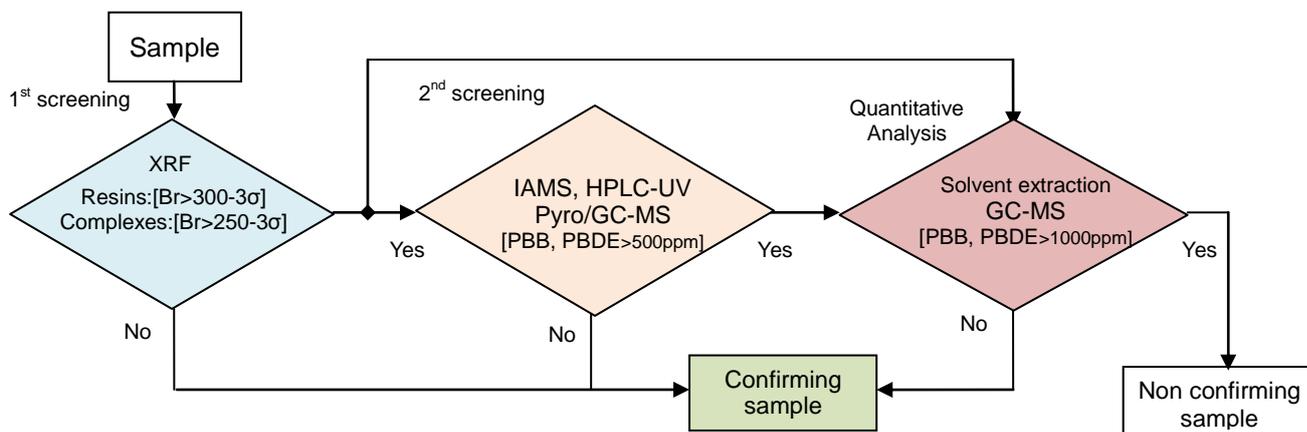


Figure-2 Flow chart on analysis method on the 2nd screening for PBBs and PBDEs.

(3) Quantitative analysis of lead and cadmium [in conformance with IEC62321 Article 8 – Article 10]

Analysis methods differ between surface-treated items such as plated ones and other homogeneous materials. Therefore, according to the purposes, analysis methods should be selected.

(3)-A. Surface-treated material such as plating

1) Surface treated material such as commonly-used plating etc.

Only the surface-treated layer of a plated test sample is selectively ground and dissolved, and is extracted as a homogeneous material, and the liquid in which it is dissolved, after being weighed, in an enclosed system (microwave decomposition) or an open system (acid decomposition) depending on the test sample is used for its analysis.

The solution of the test sample is quantitatively determined with an atomic absorption spectrometry (a flameless atomic absorption spectrometry is also available) or ICP emission spectrometry (ICP mass analysis is also available). Select acid suitable for the testing material using Table-4 as a guide.

Table-4. Recommended acid by test sample material

Test sample material	Acids
Fe, Cu, Al, Solder	Aqua regia, HNO ₃ , HCl, HF, H ₂ O ₂
Au, Pt, Pd, Ceramic	Aqua regia
Polymer	H ₂ SO ₄ , H ₂ O ₂ , HNO ₃ , HCl
Glass	HNO ₃ , HF
Ag	HNO ₃
Others	Various acid

2) Surface treated material whose plated layer is 0.1µm or less and surface area is 10mm² or less

As a company standard, analysis method 3-(B) is applicable

EU Commission accepts alternative method on an exemption as stated in RoHS Enforcement Guidance Document (*3), in case that a analysis is economically and technically difficult when huge test material is required to dissolve selectively its plated portion to make analysis in ppm basis for such test material that plated in extremely small area and at extremely thin.

*3: RoHS Enforcement Guidance Document Ed.1, (2006/05)

3) Neither of the methods above is possible to apply, because its plated portion is too small area and thick

The analysis of object substance concentration within a plating bath is applicable.

Standard control concentration shall be 1/100 of RoHS's allowable concentration.

(Cadmium is 1ppm or less, and lead is 10ppm or less)

(3)-B. Homogeneous material, such as solder, resin, paint, ink, and pigment

- The liquid in which the test sample is dissolved, after being weighed, in an enclosed system (microwave decomposition) or an open system (acid decomposition) depending on the test sample is used for its analysis.
- The solution sample is quantitatively determined by using an atomic absorption spectrometry (a flameless atomic absorption spectrometry is also available) or ICP emission spectral analysis. (ICP mass analysis is also available) You can select acid in response to material quality. (Reference Table-4)

(4) Quantitative analysis of mercury [in conformance with IEC62321 Article 7]

- The liquid in which the test sample is dissolved, after being weighed, in an enclosed system (microwave decomposition) or an open system (acid decomposition) depending on the test sample is used for its analysis. If a test sample residue remains failing to be completely dissolved, make sure that there is no mercury in the residue by XRF or other method.
- The solution of test material is quantitatively determined by using an atomic absorption spectrometry (a flameless atomic absorption spectrometry is also available) or ICP emission spectral analysis (ICP mass analysis is also available).

**(5) Quantitative analysis of hexavalent chromium compound
[in conformance with IEC62321 Annexes B and C]**

Analysis methods differ between chromate-treated components and other materials. Therefore, according to the purposes, analysis methods should be selected.

**(5)-A. Components subjected to chromate treatment on the metal surface
[In conformance with IEC62321 Annex B],**

“Boiling water (or hot water) extraction - diphenylcarbazide absorption photometry method”

- Take a sample having a surface area of 50cm² (20 - 30cm²), and perform extraction for 10 minutes by immersing the sample in 100 °C (80 °C) boiling water (hot water).
- After extraction, remove the sample, add water to the extraction liquid to make 50ml (30ml), and carry out analysis using this solution.
- For the sample solution, selectively quantify only the hexavalent chromium, using the diphenylcarbazide absorption photometry method or ion chromatograph analysis method.
- From the extracted amount measured in the preceding step and the surface area of the sample, calculate the extracted amount of hexavalent chromium (Cr⁶⁺) µg/cm².

Although IEC62321 prescribes the boiling water extraction method, boiling water can pose a high risk of burns. Therefore, application of the hot water extracting method that is our conventional analysis method [Ver.1.2] is also allowed only for in-house measurement (including business partners).

Table-5 shows the comparison of extraction conditions between both methods.

Table-5. Comparison of conditions between boiling water extraction method and hot water extraction method (*4)

Items	Boiling water extraction method	Hot water extraction method
Extraction water temperature (°C)	100	80
Extraction time (minute)	10±0.5	10±0.5
Surface area of the sample (cm ²) (*4)	50±5	25±5
Extraction water volume (ml)	50	30
Extraction efficiency (%)	100	50

*4 In the test method mentioned above, the measurement result is obtained by $(Cr^{6+})\mu\text{g}/\text{cm}^2$. To determine RoHS conformity, it is necessary to calculate the concentration in the chromate coating by determining the thickness of the chromate coating, the specific gravity of the chromate coating, the extraction efficiency, etc. However, it is considered that the chromate coating has a complicated multinuclear complex structure and conversion to the concentration in the chromate coating is very difficult because the thickness of the chromate coating and the specific gravity of the chromate coating vary with temperature and humidity. Therefore, even IEC62321 merely sets the criterion to determine the presence or absence of Cr^{6+} to $0.02\mu\text{g}/\text{cm}^2$, and does not define a criterion of judgment for conformance to RoHS standard (1,000ppm). When assuming the coating thickness to be $0.25\mu\text{m}$, the specific gravity of the coating to be 4, and the extraction efficiency to be 100% for convenience sake, the concentration in the chromate coating of $0.02\mu\text{g}/\text{cm}^2$ is estimated to be 200ppm. From this estimation, this guideline sets the criterion for RoHS conformance to $0.1\mu\text{g}/\text{cm}^2$ when measured using boiling water extraction method ($0.05\mu\text{g}/\text{cm}^2$ for hot water extraction method assuming the extraction efficiency to be 50%).

*5: As for calculation of the surface area of a screw, please refer to the surface area calculation formula shown in IEC62321 Annex B or the surface area calculation formula by the schematic diagram and the approximation formula as follows.

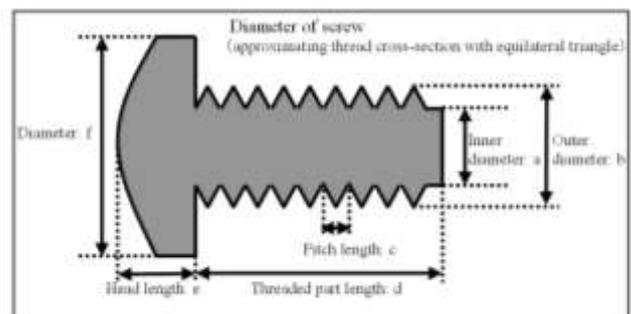
(Approximation formula)

When the cross section of threads is approximated with equilateral triangle, the surface area is given by the following formula.

Total surface area of screw = (1) Surface area of screw head and bottom + (2) Surface area of threads

$$(1) = \pi \times f \times e + 2 \times \pi \times \left(\frac{f}{2}\right)^2$$

$$(2) = \pi \times \left\{ \left(\frac{b}{2}\right)^2 - \left(\frac{a}{2}\right)^2 \right\} \times \frac{d}{c} \times 2 \times \frac{2}{\sqrt{3}}$$



(5)-B. Homogeneous material, such as resin, paint, ink, and pigment and electronic parts

[in conformance with IEC62321 Annex C]

“Alkaline extraction – diphenylcarbazide absorptiometrical method”

- Smashed test samples which pass through a screen (250µm) shall be used for analysis. After weighing them, perform extraction using alkaline/hot water.
- After extraction, remove the test samples from alkaline water and adjust the alkaline water to pH7.5±0.5 with diluted nitric acid, and then use it as a sample solution.
- Quantify only the hexavalent chromium in the solution sample using the diphenylcarbazide absorptiometrical method.
- Convert the quantifying result to the hexavalent chromium content in homogeneous material (Cr⁶⁺) µg/(the total mass of test samples)g.
- A method by which the above-mentioned extraction sample is subjected to ICP measurement and the total chromium concentration is found to be lower than the criterion value is also available.

The extraction efficiency of hexavalent chromium depends heavily on the kind of resin. Therefore, Table-6 shows the extraction methods according to the kind of resin.

Table-6. Applicability for Alkaline extraction method

Resin materials	Applicability
PVC, ABS	Allowed
EVAC, PE	Not allowed
Others	Seek the extraction efficiency experimentally and correct.

(6) 2nd Screening and Quantitative Analysis of PBBs and PBDEs in Resins

[in conformity to Draft of IEC62321 Ed2 Part 6]

The sample that is judged as being in gray zone by 1st screening is better to be analyze by quantitative analysis. It is allowed that you can implement 2nd screening before quantitative analysis, and then do the quantitative analysis after being judged as gray zone by the result of 2nd screening.

Pyro/GC-MS, IAMS or HPLC-UV can be used for 2nd screening analysis of PBBs and PBDEs

Prepare the sample for 2nd screening (different from the each equipments)

- Pyro/GC/MS, IAMS:
 - Test samples crushed under 500µm shall be used for analysis.
- HPLC-UV
 - Test samples crushed under 500µm shall be extracted by appropriate organic solvent for dissolving the sample (e.g. toluene, tetrahydrofuran).
 - Appropriate extraction procedure such as soxhlet extraction method. Test samples are either dissolution or swelling.
 - The extracted test material is cleaned up by dry silica gel and used to be analyzed.

The judgment of gray zone by 2nd screening is obeyed this formula.

$$500\text{ppm} < \text{The analyzed results of PBBs, PBDEs}$$

Prepare the sample for quantitative analysis and analyze

- Test samples crushed under 500µm shall be extracted by appropriate organic solvent for dissolving the sample (e.g. toluene, tetrahydrofuran).
- Appropriate extraction procedure such as soxhlet extraction method. Test samples are either dissolution or swelling.
- The extracted test material is cleaned up by dry silica gel and used to be analyzed.
- The extracted solution of test sample is quantitatively determined by using quadrupole GC-MS (Gas Chromatography Mass Spectroscopy analysis) equipment or magnetic sector-type high resolution mass spectrometer.

<Contact information and address >

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Abbreviations

ICP-OES: Inductively coupled plasma optical emission spectrometry

ICP-MS: Inductively coupled plasma mass spectrometry

CV-AAS: Cold vapour atomic absorption spectrometry

CV-AFS: Cold vapour atomic fluorescent spectrometry

AAS: Atomic absorption spectrometry

UV-Vis: Ultraviolet and visible spectrometry

GC-MS: Gas chromatography - mass spectrometry

IA-MS: Ion attached mass spectrometry

Pyro/GC-MS: Pyrolyzer/GC-MS

HPLC-UV: High performance liquid chromatography- Ultraviolet and visible spectrometry