Guideline regarding analysis on Fujitsu Group specified chemical substances

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Fujitsu Limited

1. Objective

Responding to requirements for compliance with regulations regarding hazardous substances in electrical and electronic equipment such as EU RoHS directive, Fujitsu Group has issued and provided “Guideline Regarding Non-Containment Management on Fujitsu Group Specified Chemical Substances”, which is a guideline on how to control Fujitsu specified chemical substances.

In addition to the “Non-Containment Guideline”, the first edition of “Guideline Regarding Analysis on Fujitsu Specified Chemical Substances” was also issued in August, 2005, which only the Japanese version was given at that time, in order to define analysis conditions and to clarify requirements when Fujitsu Group requests suppliers to provide analysis data of materials.

In this revision, especially, analysis methods are revised in view of the publication of IEC 62321 which is the International Standard related to this document.

2. Reporting Contents

The following information shall be included in a laboratory analysis report.
The report shall be submitted in a PDF file.

a) Analysis laboratory/agency
  - Name, Address
  - Name of operator who analyzes, and responsible person
  - Date of analysis (also note the date that specimen is received, if possible)

b) Applicant (who applied for analysis)
  - Applicant’s name, company, title

c) Specimen
  - Types of specimen and portion to be analyzed (e.g. description of metal, resin or chromate, and its picture)
  - Model name or number of a component (Specify Lot number if possible)
  - Target substances in the specimen to be analyzed

  Note: In case that a specimen consists of several materials, specify the above-mentioned information by each material. (However, it is not necessarily to separate the report.)

d) Analysis method and equipment
  - Method (Specify an applicable number in standards or criteria that should be applied to the analysis, if there is.)
  - Lower limit of detection

e) Preparation method
  - “Reporting items” specified in each subsection of section 3 “Recommendation on analysis method”

f) Concentration
  - “Reporting items” specified in each subsection of section 3 “Recommendation on analysis method”
  - All analysis results and their average, if specimen is analyzed more than one time.

3. Recommended analysis method

Upon the submission of evidence for analysis required by Fujitsu group, ensure to follow the analysis process specified hereafter.

3.1 X-ray fluorescence spectrometry for Pb, Cd, and Hg in metal

a) Scope
Pb, Cd, Hg in metal

b) Outline
After confirming main constituents by a qualitative analysis, analyze Pb, Cd and Hg.
With taking into account the detection accuracy, in case that each content may exceed values in table 3.1-1, implement the chemical analysis specified in section 3.3 (Note 1).

Table 3.1-1 Maximum content

Material	Lead	Cadmium	Mercury
Fe alloy	0.35wt%	0.01wt%	0.1wt%
Al alloy	0.4wt%		
Cu alloy	4.0wt%		
Other	0.1wt%		

c) Notice
Separate the surface coating, plating, or painting from the metal surface and directly analyze the target metal.
The thickness of specimen shall be no less than 2.0mm for Al alloy and Mg alloy, and 0.5mm for other metal (Note 2). Pile several specimens if single specimen does not reach the thickness required.

d) Method
Use an X-ray fluorescence spectrometer that complies with the requirements in JIS K0119 (*). In addition, the spectrometer/analyzer shall have detection limit of 0.01wt%(100ppm) or better for Pb and Hg, and 0.005wt％（50ppm） or better for Cd. After confirming the main constituents by qualitative analysis, analyze Pb, Hg and Cd.
In case of an analysis using a working curve, the curve shall fulfill either of the followings:

1) it is made based on standard samples whose main constituents are similar to specimen subject to analysis, or
2) it is made based on specimens whose concentrations are clarified by means of chemical analysis.

(*)JIS: Japanese Industrial Standards

e) Reporting items

- Picture of portion where is measured. (Portion of X-ray irradiation shall be clarified.)
- Quantitative analysis method (FP method or Calibration curve method)
- Analysis result (Main constituents, Quantitative values of Pb, Cd and Hg, and σ.)
- Spectrum of fluorescent X-ray of specimen (Entire spectrum, and spectrum focusing around the peaks of Pb, Cd and Hg)

Note 1, In the case the estimated content of Pb or Cd is around the maximum content in Table 3.1-1, implement chemical analysis specified in 3.3. Such chemical analysis is not required if conditions below are satisfied.
- It is possible to attach both a spectrum and measurements of chemical analysis of concentration-known specimen that contains Pb or Cd of concentration around the maximum content (e.g. In case of Cu alloy, brass that contains Pb around 4wt% and Cd around 0.007wt%(70ppm)).
- Target specimen contains Pb or Cd less than the maximum content, after target specimen is calibrated using the concentration-known specimen described above.

Note 2 IEC 62321 requires the thickness of 5 mm and 1 mm respectively. But this document moderate the demand for the thickness based on past results.

3.2 X-ray fluorescence spectrometry for Pb, Cd, Hg, Total Cr and Total Br in resin, etc.

a) Scope
Pb, Cd, Hg, Total Cr and Total Br in resin, coating or ink

b) Outline
After confirming all elements composition (except for light elements) by a qualitative analysis, analyze Pb, Hg, Cd , total Cr and total Br by a working curve method using an appropriate filter. With taking into account the detection accuracy, implement the chemical analysis specified in section 3.4 (*), in case that each content may exceed 0.01wt% for Cd, 0.1wt% for Pb and Hg.
It is not necessary to do Cr6+ analysis required in 3.7, if the content of total Cr is obviously less than 0.05wt%. Neither is GC-MS analysis required in 3.8, if the content of total Br is obviously less than 0.03wt%.

c) Notice
Separate the surface finish, plating, or coating from the surface of the target resin and directly analyze it.
The thickness of specimen shall be no less than 2.0mm (Note 1). Pile several specimens to reach the thickness required, if necessary.

d) Quantification Method
Use an X-ray fluorescence spectrometer that complies with the requirements in JIS K0119. In addition, the spectrometer/analyzer shall have detection limit of 0.01wt% or better for Pb, Hg, total Cr and total Br, 0.005wt%(50ppm) or better for Cd.
In case of analysis using a working curve, the curve shall fulfill either of the following (Note 2):

1) it is made based on standard samples whose main constituents are similar to specimen subject to analysis, or
2) it is made based on specimens whose concentrations are clarified with chemical analysis by plural analysis laboratories.

If an analyzer enables to calibrate the influence caused by coexisting elements, it is allowed to use concentration-known specimens with different elements composition unless the calibration is done out of the available extent regarding kinds of element and range of concentration.
After confirming main constituents by a qualitative analysis, implement a quantitative analysis by a calibration curve method using an appropriate filter, for Pb, Hg, Cd, total Cr, and total Br.

e) Reporting items
- Picture of portion where is measured. (Portion of X-ray irradiation shall be clarified.)
- With or without calibration: (Types of calibration, e.g. forms, coexisting elements)
- Analysis result (Quantitative values of Pb, Hg, Cd, total Cr, and total Br, and σ)
- Spectrum of fluorescent X-ray of specimen (Entire spectrum, and spectrum focusing around the peaks of Pb, Cd Hg, Cr and Br)
- Estimated quantity of the solvent, if specimen contains. (e.g. coating or ink)

Note 1; IEC 62321 requires the thickness of 5 mm. But this document moderate the demand for the thickness based on past results.

Note 2; Though the certified reference material (CRM) or reference material (RM) are desirable for making the working curve, CRM and RM are often unavailable. Therefore in this document the demands for reference materials are moderated.

3.3 Chemical analysis for Pb, Cd, Hg in metal

a) Scope:
Pb, Cd, Hg in metal

b) Outline
Determine Pb, Cd, Hg in resin in conformity to IEC 62321 chapter 7 or chapter 9 (Note 1). Dissolve the specimen in acid, and quantitatively analyze the solution by means of either ICP-AES, ICP-MS with using a working curve obtained by using working solution. CV-AAS or AFS is also recommended for analysis of Hg. AAS is also recommended for analysis of Pb and Cd.

c) Sample preparation
Dissolving the specimen shall be performed in accordance with the following ways. Any deposit (insoluble matter) shall not be allowed. In case of difficulties in completely dissolving the specimen, it is necessary to secure that Pb, Cd and Hg be not contained in the deposit, by means of X-ray fluorescence spectrometry, etc.

- Pb and Cd; IEC 62321 chapter 9.4
- Hg; IEC 62321 chapter 7.4

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d) Method

- Pb and Cd; IEC 62321 chapter 9.6
- Hg; IEC 62321 chapter 7..5

e) Reporting items

- Sample preparation methods (e.g. conditions for the dissolving, and presence or absence of deposits)
- If a deposit is observed: an analysis method applied to the deposit, and its result
- Actually analyzed values of the following parameters used in the calculation of the content per weight.
  Parameters:
  - Initial weight of the specimen
  - Final quantity of the solution
  - Concentration of the specimen in the final solution

<u>Abbreviations</u>:
- ICP-AES (ICP-OES) : Inductively Coupled Plasma Atomic Emission Spectroscopy
- ICP-MS : Inductively Coupled Plasma Mass Spectroscopy
- AAS : Atomic Absorption Spectroscopy
- CV-ASS : Cold Vapor Atomic Absorption Spectroscopy
- AFS : Atomic Fluorescence Spectroscopy

Note 1; For the time being, a report based on EN ISO 11885, JIS K0116 (ICP-AES)、EN ISO 172941-1, JIS K0130 (ICP-MS) and EN ISO 5961 (AAS), which were recommended in Edition 2.0 of this guideline, is also acceptable.

3.4 Chemical analysis for Pb, Cd, Hg in resin

a) Scope:
Pb, Cd, Hg in resin, coating, or ink

b) Outline
Determine Pb, Cd, Hg in resin in conformity to IEC 62321 chapter 7 or chapter 8 (Note 1). Dissolve the specimen in acid, and quantitatively analyze the solution by means of either ICP-AES, ICP-MS with using a working curve obtained by using working solution. CV-AAS or AFS is also recommended for analysis of Hg. AAS is also recommended for analysis of Pb and Cd.

c) Sample preparation
Dissolving the specimen shall be performed in accordance with the following ways. Any deposit (insoluble matter) shall not be allowed. In case of difficulties in completely dissolving the specimen, it is necessary to secure that Pb, Cd and Hg be not contained in the deposit, by means of X-ray fluorescence spectrometry, etc.

- Pb and Cd; IEC 62321 chapter 8.4
- Hg; IEC 62321 chapter 7.4

d) Method

- Pb and Cd; IEC 62321 chapter 8.5
- Hg; IEC 62321 chapter 7..5

e) Reporting items

- Sample preparation methods (e.g. conditions for the dissolving, and presence or absence of deposits)
- If a deposit is observed: an analysis method applied to the deposit, and its result
- Actually analyzed values of the following parameters used in the calculation of the content per weight.
  Parameters:
  - Initial weight of the specimen
  - Final quantity of the solution
  - Concentration of the specimen in the final solution
- Estimated amount of the solvent in the specimen if it is contained (e.g. in case of coating, or ink)

<u>Abbreviations:</u>

- ICP-AES (ICP-OES)	: Inductively Coupled Plasma Atomic Emission Spectroscopy
- ICP-MS	: Inductively Coupled Plasma Mass Spectroscopy
- AAS	: Atomic Absorption Spectroscopy
- CV-ASS	: Cold Vapor Atomic Absorption Spectroscopy
- AFS	: Atomic Fluorescence Spectroscopy

Note 1; For the time being, a report based on EN ISO 11885, JIS K0116 (ICP-AES)、EN ISO 172941-1, JIS K0130 (ICP-MS) and EN ISO 5961 (AAS), which were recommended in Edition 2.0 of this guideline, is also acceptable.

3.5 Chemical analysis for Pb, Cd in plating film

Generally, an analysis of a small amount of constituents in a plating film is very expensive and difficult. From the cost point of view, it is highly recommended to create a test piece for the analysis objective. In this case, the top surface of a substrate (where the plating film starts growing) of the test piece shall be equivalent to that of the actual specimen. Also, plating equipment, plating solvent composition and process conditions shall be equivalent to the actual production process of the relevant component/devices.

- In case of an analysis of actual components/devices:
  Please submit evidence that demonstrates technical adequacy.
- In case of an analysis other than the chemical analysis (e.g. Glow Discharge mass spectroscopy, etc):
  Please consult with our contact person in a technology division.

a) Scope

Pb, Cd in plating film

b) Outline

Conduct chemical analysis for Pb and Cd by means of either of the following methods (1) through (3) specified in c) below. The chemical analysis method used herein shall conform to “Chemical analysis for Pb, Cd, and Hg in metal” in 3.3.

c) Specimen, Calculation of the concentration, and Reporting items

(1) Quantification by subtraction: acquiring difference in measurements between a specimen with a plating film and base metal without the plating film

- Divide a specimen into two pieces, and prepare the 2 types of the specimen: one with a plating film and the other without the plating film (remove the plating film by grinding, etc). Conduct chemical analysis according to the 3.3, and measure the Pb and Cd concentration. Calculate the difference between two measurements obtained, for the concentration of Pb and Cd respectively.
  Generally, it is expected that a maximum margin of error in measurements of a substrate is about 10% (including variation within the specimen). On account of this, a test piece provider shall use a thin substrate containing little amount of Pb and Cd that assures no more than 0.005wt%(50ppm) for Pb and 0.001wt%(10ppm) for Cd in concentration when estimated as concentration margin of error in the plating film .
  For example,
  Approximation of concentration in case of an iron board of 1mm thickness having a Ni-P plating film of 2μm thickness on its both sides:
  Since an approximate weight ratio of the iron board to the plating film (Note: assumable as Ni films) is 250:1, the ‘50 ppm error’ for Pb in the plating film corresponds to ‘0.2ppm error’ in the iron board. As this value corresponds to ‘10% error’ for the iron board, the Pb concentration in the iron board shall be no more than 2ppm. In the same way, the Cd concentration shall be no more than 0.4ppm.

Reporting items:

- Type of substrate (base metal) of the analysis specimen
- Thickness of plating film and substrate respectively
- All measured values used to calculate concentrations
- Other information that is specified in 3.3

(2) Quantification after dissolving only the plating film

- Applicable specimen:
  A specimen whose plating film is exclusively dissolvable (anything other than the plating film shall not be dissolved) and its substrate does not contain Pb, Cd and other main constituents of the plating film. (e.g. A Sn plating film over a Cu lead frame)
- After the plating film is exclusively dissolved, conduct a chemical analysis according to 3.3. Main constituents of the plating film and the substrate shall be quantitatively analyzed. In case of elution of the substrate being inevitable, ratio of a metal element eluted to that of the plating film shall be no more than 1wt%.

The following equation shall be used to calculate the Pb and Cd concentration in the plating film;

Pb or Cd concentration =

$$\frac{\text{(Quantity of Pb or Cd)}}{\text{(Quantity of all elements detected – Quantity of elements eluted from the substrate)}}$$

Reporting items:

- Type of substrate (base metal) of the specimen
- All measured values used to calculate concentration, and amount of eluted substrate
- Other information that is specified in 3.3

(3) Analyze plating film after removing base metal

- Applicable specimen:
  A specimen whose plating film does not elute although its substrate does (e.g. NiP plating film over Al material)
- Dissolve the substrate exclusively and conduct a chemical analysis according to 3.3. Main constituents of the plating film and the substrate shall be quantitatively analyzed. In case the substrate cannot be completely removed, the amount of a target element eluted from the substrate shall not exceed 1% of that of in the plating film.

3.6 Test for the presence of hexavalent chromium (Cr6+) in chromate coating

a) Scope:
Cr6+ in chromate coating over a metal surface, and an anodic oxide film.

b) Outline
As the technology to quantitatively analyze Cr6+ in a surface film has not reached the practical level, check presence or absence of Cr6+ elution by the following methods and make judgment on Cr6+ content.

c) Sample preparation (Extract Cr6+)
Boiling-water extraction method, according to Appendix 2 of JIS H8625. (The standard in the public announcement No. 13 issued by Japanese Environment Agency is unacceptable.) The method according to IEC 62321 annex B 5.2 is also acceptable.

> Size of Specimen: Basically, create and use a piece of specimen with surface dimension of $50cm^2$. A specimen sampled from an actual component/device is also available if the detection limit of $0.01\mu g/cm^2$ is assured with the surface dimension of no less than $10cm^2$.

d) Quantitative Method
Either diphenylcarbazide absorption spectroscopy, ion chromatography, or iron coprecipitation separation - ICP-AES is available as long as Cr6+ in the extracted solution can be isolated and quantitatively analyzed. (e.g. EPA 7199A, EPA 7168A, JIS K0400-65-20, etc)

e) Reporting items
- Actually analyzed values of the following parameters used to calculate the quantity of the elution per surface dimension
  Parameters:
  - Surface dimension of the chromate film
  - Final quantity of the solution extracted
  - Cr6+ concentration in the final solution

3.7 Test for the presence of hexavalent chromium (Cr6+) in resin, etc (Note 1).

a) Scope:
Cr6+ in resin, paint, ink and packaging material
(Analyze paint / varnish in case of a coating.)

b) Outline
As the absence of an analytical technology which a specimen can be completely dissolved without changing the status of Cr6+, check presence or absence of Cr6+ elution by the following methods and make judgment on Cr6+ content.
The Cr6+ analysis defined herein is not necessarily conducted, if total Cr concentration is no more than 0.05wt% (corresponding weight under dried condition in case of solvent) confirmed by the X-ray fluorescence spectrometry using a calibration curve method specified in 3.2.

c) Sample preparation (Extract ion of Cr6+)
Apply the alkaline extraction method according to EPA 3060A. If the sample is solution, put it on a plate and dry it, where the plate can be removed after the solution has dried, so the specimen should be in an approximate condition of actual usage. The specimen shall be grinded until the diameter of each grinded piece becomes less than 0.25 mm by means of cryogenic grinding, etc. At least 2.5g is required for the subsequent extraction process.

d) Quantification Method
Either diphenylcarbazide absorption spectroscopy (Note 2), ion chromatography, or iron coprecipitation separation - ICP-AES is available as long as Cr6+ in the extracted solution can be isolated and quantitatively analyzed. (EPA 7199A, EPA 7168A, JIS K0400-65-20, etc)

e) Reporting items
- Actually analyzed values of following parameters used to calculate the quantity of elution per surface dimension
  Parameters:
  - Surface dimension of chromate film
  - Final quantity of the solution extracted
  - Cr6+ concentration in the final solution

Note 1; This chapter is described as a “Test for presence”, though IEC 62321 annex C is described as a “Determination”.

Note 2; Diphenylcarbazide absorption is sometimes interfered by coexisting substances. In case of difficulty in obtaining proper results due to the coexisting substances, coprecipitation method by ferric hydroxide or other method shall be applied.

3.8 GC-MS analysis for PBB/PBDE in plastic

a) Scope:
Polybrominated Biphenyl (PBB), or Polybrominated Diphenyl ether (PBDE) in plastic

b) Outline
After sample preparation completed, analyze the solution extracted by means of GC-MS, and compare retention times and mass spectral patterns with those of standard samples to judge presence or absence of PBB/PBDE according to IEC 62321 annex A (Note 1). If the content of total Br is no more than 0.03wt% confirmed by the X-ray fluorescence spectrometry using a calibration curve method specified in 3.2, GC-MS analysis is not necessarily conducted.

c) Data library of standard samples
It is essential to have a data library in which retention times and mass spectra of standard substances, for PBB and PBDE respectively are stored.
The followings are available as standard samples:

A) PBB compound (A compound of several types of brominated biphenyls), and PBDE compound (the same as PBB)
B) Single substance: At least 5 standard substances (Tetra to Deca BB/BDE) shall be prepared, for PBB and PBDE respectively. Ensure to include Deca BDE in the library.

d) Sample preparation (Extraction of PBB/PBDE and clean up)
To extract PBB/PBDE, grind a specimen into fine pieces less than 0.5 mm and take no less than 0.1g. Then, make it dissolve or swell using an organic solvent such as tetrahydrofuran. In case of difficulty in dissolving or swelling the specimen, apply the frost shattering method to obtain the powdery specimen with diameters less than a few μm, and apply the Soxhlet extraction method (for 6 hours or more, or, 20 cycles or more) using toluene, etc.

e) Reporting items

- Type (compound, or single substance) and number of standard samples registered in the data library
- Condition of specimen under extraction process (dissolved or swelled). Description of the solvent in case of Soxhlet extraction applied.
- The ion chromatogram or the mass chromatogram of the specimen (If 6 months have not been elapsed after the analysis date, when data submission is required, ensure to submit the each mass spectrum in the chromatogram.)
- The mass chromatograms of both the standard sample and that of the relevant constituent of the specimen if they have the same retention time.

Note 1; Surrogate is not always essential when the accuracy is guaranteed periodically using a reference material.
Internal standard is not essential when the amount of injection is fixed by auto sampler.

3.9 Chemical analysis of packaging materials

a) Scope:

Pb, Cd, Hg, Cr6+ in packaging materials such as corrugated boards, tape, wooden frame, plastic container, etc. As for print on packages, analyze the ink before being printed on the packages.

b) Outline

Conform to the regulation based on “European Parliament and Council Directive 94/62/EC of 20 December 1994 on packaging and packaging waste”, and ensure that the total amount of Pb, Cd, Hg and Cr6+ detected from a specimen of the packaging materials is no more than 0.01wt% in concentration.

Determination of Pb, Cd, Hg shall be based on IEC 62321 chapter 7 or chapter 8. IEC 62321 chapter 8 can be applied for determination of total Cr,

Implement “Analysis of Cr6+ in resin” specified in 3.7, if the result meets both of the following scope:

- Total amount of Pb, Cd, and Hg <0.01wt%, and, Pb, Cd, Hg and Cr >0.01wt%

c) Sample preparation

Dissolve the specimen, which is cut or grinded, by the method of closed system acid decomposition. Any deposit (insoluble matter) should not be allowed. In case of difficulties in completely dissolving the specimen, it is necessary to secure that Pb, Cd, Hg, and total Cr be not contained in the deposit, by means of X-ray fluorescence spectrometry, etc.

- Acidolysis method (e.g. EPA SW-846 method 3050B)
- Wet digestion method (BS EN 112, etc)
- Pressurized acidolysis within sealed container (Including micro wave method: EPA3052), etc

Remarks about a sample:

Take the portion without printing. It is essential to analyze ink separately, if the package has any printing on it.

d) Method

Measure content of Pb, Cd, Hg and total Cr by the following methods:

- Pb and Cd; IEC62321 chapter 8.5
- Hg; IEC62321 chapter 7.5

e) Reporting items

- Sample preparation methods (e.g. type of acid used for dissolving, and presence or absence of deposits)
- If a deposit is observed: an analysis method applied to the deposit, and its result.
- Actually analyzed values of following parameters used in the calculation of the content per weight.

  Parameters:
  - Initial weight of specimen
  - Final quantity of solution
  - Concentration of the specimen in the final solution
- Analysis details specified in 3.7, if “Analysis of Cr6+ in resin” is otherwise conducted.

* If packaging material has any printing on its surface, analysis data on each ink may be otherwise required.

Revision history

2005 Aug 1st	(Ver.1)	Initial edition
2007 May 1st	(Ver.2)	Revised the content, partially.
2009 June 29	(Ver.3)	Revised the content, partially.