

# Efficient and Unique System for Verifying Containment of Hazardous Substances

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The European Union's directive on the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment (RoHS) prohibits the use of certain hazardous substances. One of the targets of our environment protection program is to eliminate these substances from all Fujitsu brand products by the end of March 2006. To achieve this target, we are promoting green procurement and non-containment verification of these substances. We have developed a unique system to efficiently verify that several hundred thousand types of parts composed of various materials do not contain the RoHS-prohibited substances. This system has two elements. One is a substance containment probability chart that is based on an investigation of situations in which those substances are used. The other is a high-accuracy quantitative technique that uses simple X-ray fluorescent (XRF) spectrometry. This system enables us to efficiently verify non-containment by screening parts that have a high substance-containment probability and then accurately measuring substance concentrations using XRF spectrometry.

## 1. Introduction

Global environmental problems such as the depletion of fossil fuels; global warming due to CO<sub>2</sub>; and the pollution of air, water, and soil are increasingly difficult to ignore. The EU has taken the initiative by issuing the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment (RoHS) directive in February 2003. The RoHS directive prohibits the use of lead (Pb), mercury (Hg), cadmium (Cd), hexavalent chromium (Cr VI), and two types of brominated flame retardants — polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs) — in electronic and electrical equipment starting July 1, 2006. Because these are high-performance, high-reliability substances, they have been used over many years, and their substitution is not easy. Therefore, this directive is having a big impact on electrical and electronic industries.

The Fujitsu Group has stopped using 27 substances (including PBBs and PBDEs) that are prohibited by domestic and foreign legislations in its products. In addition, four other substances (Pb, Cd, Hg, and Cr VI) were added to this list, making a total of 31 prohibited substances. The Fujitsu Group decided to stop using these 31 substances in its products by the end of March 2006 as one of the targets of the fourth Environment Protection Program<sup>1)</sup> and made this decision public in the 2004 Fujitsu Group Sustainability Report.<sup>2)</sup>

This target can be achieved through green procurement in cooperation with suppliers, who must build and run environmental management systems and make their products conform to the hazardous-substance regulations of the Fujitsu Group. In addition, we especially need a method for verifying the compositions of new substances. Because the Fujitsu Group buys several hundred

thousand types of parts from its suppliers, it is impossible to analyze the composition of each type. Therefore, it is necessary to develop a screening method to efficiently verify the compositions of parts.

## 2. Managing non-containment of hazardous substances

Our basic concepts for managing non-containment of hazardous substances are as follows.

- 1) Source management: Every effort is made to eliminate the target substances via strict management at the material level.
- 2) Traceability: Only identified materials are used.
- 3) Management responsibility: The companies and individuals who supply items to the Fujitsu Group are responsible for verifying, by appropriate means, whether the supplied information about the contained substances is correct.

This concept was announced in the Green Procurement Direction.<sup>3)</sup> We have been managing non-containment in cooperation with our suppliers through green procurement so that parts conform to the Fujitsu Group's "Provisions for Control of Specified Hazardous Substances." However, because the supply chain is complex and global, it is very difficult to trace the source of all procured parts. Even for parts that are confirmed and guaranteed by suppliers, it is impossible to prevent them from being accidentally or otherwise contaminated with a prohibited substance during distribution.

Therefore, each electrical and electronic company verifies by voluntary analysis that their parts contain none of the prohibited substances.<sup>4)</sup> Of course, the Fujitsu Group has the ability to make such verifications by itself; however, it is impossible to verify non-containment for all of the several hundred thousand types of parts that the Group procures.

We therefore developed the following techniques for efficiently verifying non-containment:

- 1) A technique for judging the probability of containment

We determine the probability that a part contains a hazardous substance based on the reasons the substance is used and the situations in which it is used. We then identify the parts that have a high probability of containing that substance.

- 2) A technique for simple qualitative and quantitative analysis

This is an easy-to-use technique for quantitative screening analysis that, although less accurate than chemical analysis, is more accurate than conventional easy-to-use techniques.

By using these two techniques, we can reduce the use of parts that contain prohibited substances within the Fujitsu Group.

## 3. Reducing analysis person-hours by predicting containment and a simpler screening analysis<sup>5)</sup>

### 3.1 Substance containment chart

To judge whether parts contain prohibited substances, we investigated the reasons for using the substances and the situations in which they are used for the period January 2004 to June 2004. We classified substance-containment probability based on the information obtained in the investigation and made a containment probability chart for each material.

- 1) Materials that contain prohibited substances and reason for using them

We studied various documents<sup>6)</sup> obtained on the Internet and obtained information from manufacturers. We gathered information about the types of substances used in basic materials such as bulk metal, solder, plating materials, surface treatments, resins, and glass and why they were used.

- 2) Compositions and amounts of prohibited substances in standard products

The compositions and amounts of prohibited substances in most of the materials used in standard products are usually managed according to

industrial standards. We therefore referenced these standards to find out which types of materials contained prohibited substances and why they contained them.

3) Types of alternative materials and their promotion

Some substances were prohibited or restricted to limited use before they were classified as hazardous substances (e.g., lead in solder and PBBs/PBDEs). We investigated which alternatives to these substances are available and how their substitution is promoted in the market.

4) Research by analysis

We analyzed the materials of various parts and verified their containment probability. We then classified the probabilities that a material contains a prohibited substance as follows:

- 1) Contained, but being phased out.
- 2) Occasionally contained.
- 3) Rarely contained.
- 4) Basically, not contained. (No reason for the prohibited substance to be in the material.)
- 5) Never contained.

For instance, **Figure 1** shows the containment probability chart for Cd in copper ingots. Brass is classified as 1) “Contained, but being phased out.” Brass has a high probability of containing Cd because of impurities in its zinc constituent.<sup>7)</sup>

We made a containment probability chart based on the result of an investigation. **Figure 2** shows this chart. It shows, for example, that PBB/PBDE bromine system flame retardants are basically not used in thermosetting resins. Thermosetting resins, silicone resins, and fluoro-

plastics are basically flame-resistant. Therefore, flame retardants are not generally used in flame-resistant resins because there would be no advantage. In a recent survey, companies that collectively manufactured 80% of the world’s supply of PBB and PBDE flame retardants said they have not manufactured those chemicals since 2000, except for a small amount of deca-BDE — the use of which has been limited. The only place we found PBDEs in use was in the shield plastic of high-frequency cables.

### 3.2 Screening analysis flow

In general, we use X-ray fluorescence (XRF) spectrometry as a simple screening analysis technique and improved its qualitative and quantitative accuracy. We prepared various standard samples of each material that had a high containment probability, applied these samples to metal substrates (by painting, soldering, etc.), and then used the substrates to estimate the minimum limit of detection and the measuring accuracy. We made standard samples that were difficult to otherwise obtain and confirmed the amounts of prohibited substances they contained using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and other techniques. We established methods and analysis conditions, made calibration curves for determining concentrations of prohibited substances, and established criteria for judging whether materials contain prohibited substances.

**Figure 3** shows the calibration curve we made for tin-lead (Sn-Pb) solder. The curve shows the concentration of Pb in standard samples of Sn-Pb solder and the intensity of the Pb’s  $L\alpha$  ray observed in XRF spectrometry. We can accurately calculate the concentration of Pb from this calibration curve by measuring the intensity of the Pb’s  $L\alpha$  ray. **Figure 4** shows an example XRF spectrum of a resin that was used to determine the resin’s Pb concentration. Usually, we determine Pb concentration by the intensity of the Pb’s  $L\alpha 1$  and  $L\beta 1$  rays. However, we cannot determine



Figure 1  
Chart showing use of Cd in Cu ingots.

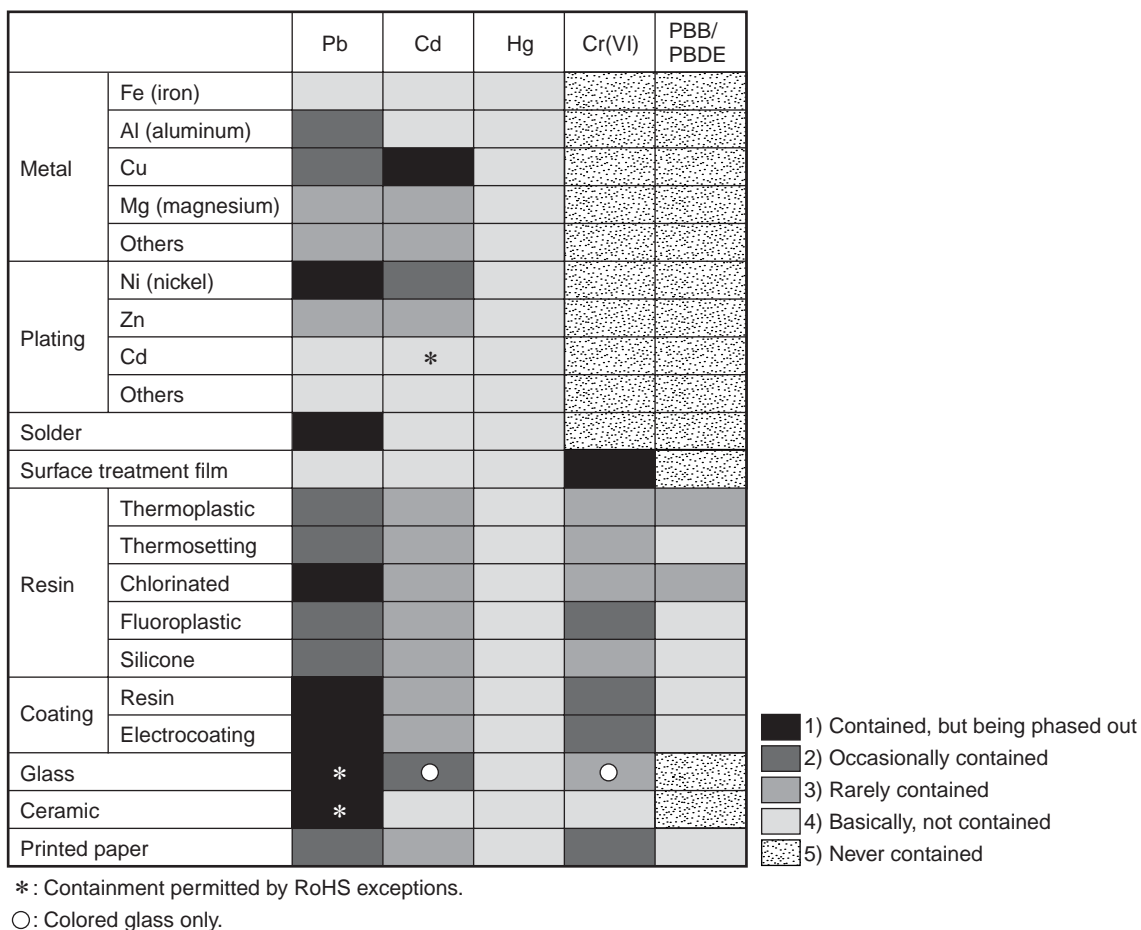


Figure 2  
Containment probability chart for RoHS-prohibited substances in various materials.

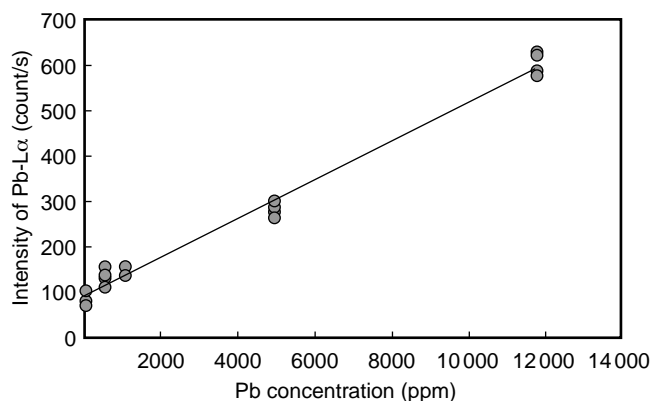


Figure 3  
Calibration curve for Pb in Tin (Sn).

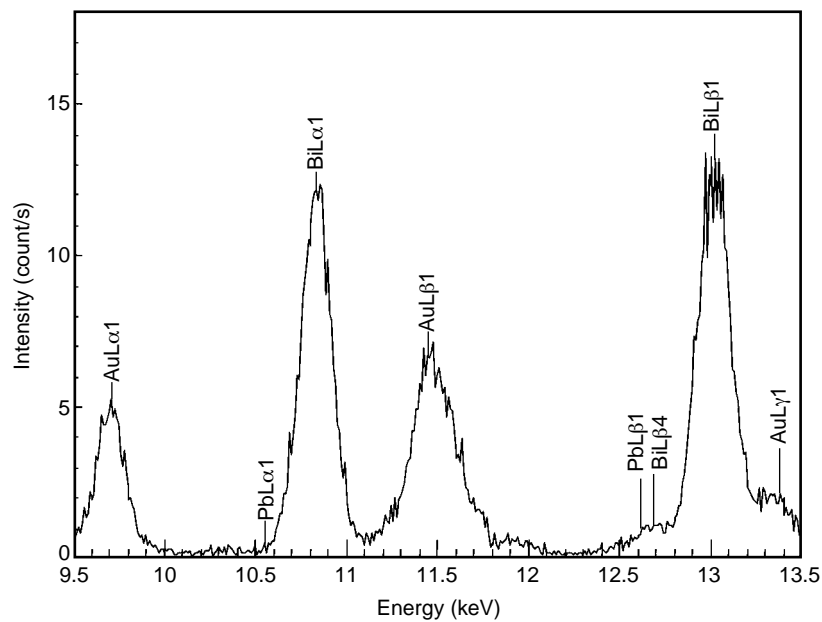


Figure 4  
Example of XRF spectrum of resin.

the concentration by the intensity of the  $L\beta_1$  ray when Bi coexists in the sample because, as can be seen in the figure, the  $L\beta_1$  ray of Pb is very close to the  $L\beta_4$  ray of Bi. In this case, we must determine the Pb concentration from the  $L\alpha_1$  ray, which is only slightly influenced by the  $L\alpha_1$  ray of Bi. From the spectrum shown in Figure 3, we can determine that this resin does not contain Pb.

**Table 1** is a list of the chrome-system inorganic pigments<sup>8)</sup> registered in the Color Index. This table shows that the pigments containing Cr VI contain either barium (Ba), zinc (Zn), strontium (Sr), or Pb. The pigments that contain Pb are prohibited. Therefore, if we detect Ba, Zn, or Sr coexisting with Cr in a sample, it is highly possible that the sample contains Cr VI. In such a case, we have to measure Cr VI quantitatively in the sample by using the colorimetric method in the dissolution test.<sup>9)</sup> Therefore, we can efficiently verify non-containment of Cr VI in the samples because we can reduce the number of samples to be measured by the colorimetric method, which is a time-consuming method. We developed these analysis procedures for measuring Cr VI and developed a procedure to efficiently verify Cr VI

containment in pigments (**Figure 5**).

As mentioned above, we developed techniques that improve the qualitative and quantitative accuracy of XRF spectrometry. These techniques enable us to efficiently verify non-containment in parts.

#### 4. Application of developed techniques

We use the techniques we developed to promote the steady elimination of prohibited substances in two ways: 1) parts specification for registration and 2) inspection of supplied parts at production sites. At registration, we confirm the non-containment information we receive from the suppliers and enter the non-containment materials in the purchase specifications. Moreover, we verify which parts materials have a high containment probability according to the developed analysis flow. When inspecting purchased parts at production sites, we judge their containment probabilities by using the substance containment probability chart and verify whether there are any parts with high containment probabilities. By using this process, we can prevent delivery of parts

Table 1  
Chromium inorganic pigments registered in Color Index.

Name	Chemical formula	Cr Valence	Pb
PY31	BaCrO <sub>4</sub>	VI	none
PY32	SrCrO <sub>4</sub>	VI	none
PY34	PbCrO <sub>4</sub> · nPbSO <sub>4</sub>	VI	coexist
PY36	ZnCrO <sub>4</sub> · 4Zn(OH) <sub>2</sub>	VI	none
PY36:1	ZnCrO <sub>4</sub> · 4Zn(OH) <sub>2</sub>	VI	none
PY118	TiO <sub>2</sub> - Cr <sub>2</sub> O <sub>3</sub>	III	none
PO21	mPbCrO <sub>4</sub> · nPbO	VI	coexist
PR104	PbCrO <sub>4</sub> · PbMoO <sub>4</sub> · PbSO <sub>4</sub>	VI	coexist
PB36	CoO - Al <sub>2</sub> O <sub>3</sub> - Cr <sub>2</sub> O <sub>3</sub>	III	none
PG15	PbCrO <sub>4</sub> · nPbSO <sub>4</sub>	VI	coexist
PG17	Cr <sub>2</sub> O <sub>3</sub>	III	none
PG18	Cr <sub>2</sub> O(OH) <sub>4</sub>	III	none
PG26	CoO - Al <sub>2</sub> O <sub>3</sub> - Cr <sub>2</sub> O <sub>3</sub>	III	none
Br24	TiO <sub>2</sub> - Sb <sub>2</sub> O <sub>5</sub> - Cr <sub>2</sub> O <sub>3</sub>	III	none
Br33	ZnO - Fe <sub>2</sub> O <sub>3</sub> - Cr <sub>2</sub> O <sub>3</sub>	III	none
Br35	Fe <sub>2</sub> O <sub>3</sub> - Cr <sub>2</sub> O <sub>3</sub>	III	none
PBk22	CuO - Fe <sub>2</sub> O <sub>3</sub> - Cr <sub>2</sub> O <sub>3</sub>	III	none
PBk28	CuO - Cr <sub>2</sub> O <sub>3</sub>	III	none

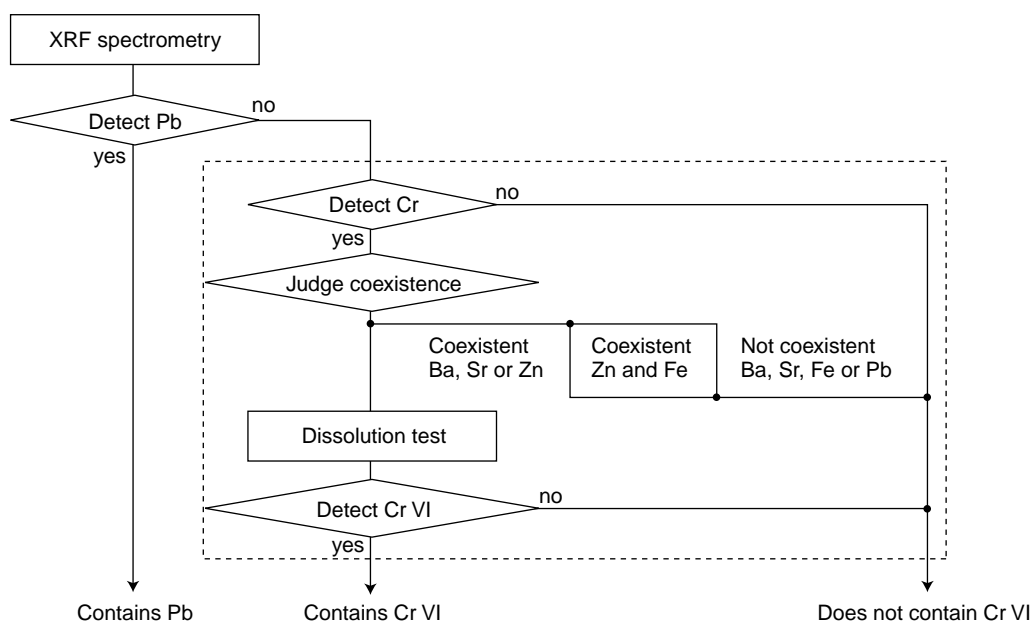


Figure 5  
Analysis flow for judging containment of Cr VI in resin.  
(Most Cr in resin is in chromium-system inorganic pigments.)

that contain prohibited substances.

In addition to the substance-containment probability chart and verification procedure, we also built a database of basic technical knowledge about previous analysis cases and the prohibited substances (**Figure 6**). We believe that this database is a useful resource for understanding the RoHS directive. This database can be accessed by Fujitsu Group companies over the Fujitsu intranet.

## 5. Future developments

The RoHS directive will have a big effect on the worldwide use of the substances that it covers, and it will be necessary to continuously check the situation and update the database to ensure effective verification of non-containment. Alternative materials and the technology for using them are being developed, and the disuse of the prohibited substances is being advanced in response to the RoHS directive. Therefore, new problems may arise as these alternative materials and technologies come into use. To solve these

problems, these new materials and technologies must be highly reliable and have a smaller environmental burden and lower cost. To achieve these goals, we must understand and clarify the properties of these materials and the reasons these problems occur theoretically. We are now addressing these problems to make good use of the advanced analysis technology that can be used to solve these new problems.

## 6. Conclusion

In this paper, we described efficient, high-accuracy, and unique screening techniques that we developed to verify whether parts contain prohibited substances. These techniques consist of the substance-containment probability chart and a high-accuracy, high-efficiency screening analysis technique that uses XRF spectrometry. This technique makes it possible to efficiently verify non-containment for several hundred thousand types of parts and thereby significantly reduce containment probability in our products.

However, although we can verify non-

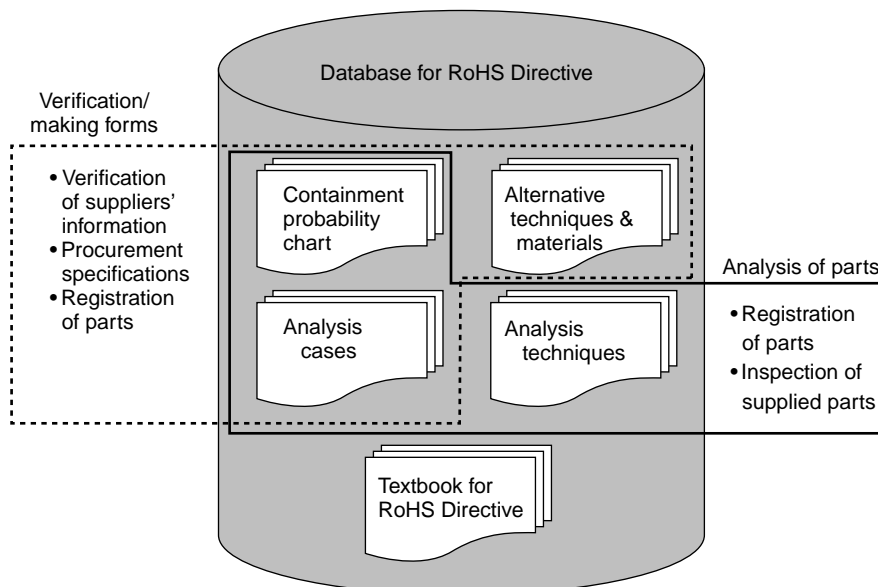


Figure 6  
Contents of technical database for RoHS directive.

containment by this technique, we cannot use it to guarantee non-containment. We believe that source management at the material level is the only means for non-containment management of prohibited substances. Therefore, it is important to seek closer cooperation with suppliers and manufacturers.

In the future, we would like to contribute to sustainable social growth by producing eco-friendly products using new analysis techniques for solving environmental problems.

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