Selected Article

Screening Analysis of Hazardous Elements using X-ray fluorescence Analyzer

— Analytical Technique in Compliance with RoHS Directive —

Atsushi Bando

Under recent circumstances where attention to the environment is required in every field, there is an increasing need for analysis of hazardous substances included in products such as electrical and electronic equipment, and automobiles, as triggered by the enforcement of the RoHS Directive of the European Union (EU). As part of this trend, the X-ray fluorescence analyzer (XRF) plays an important role as a screening apparatus for confirmation of absence of hazardous substances in parts and materials. In this article, we will introduce the outline of RoHS Directive and the actuality of screening analysis using XGT-WR series that were developed by HORIBA for analysis of hazardous substances.

Introduction

On July 1, 2006, the European Union (EU) enforced a directive for restriction of hazardous substances in electrical and electronic equipment[1] (RoHS Directive: Restriction of the use of certain Hazardous Substances). Triggered by the temporary prohibition on import of home video game machines made in Japan in the Netherlands at the end of 2001 (owing to detection of cadmium in the cables at an amount more than the permissible standard, shipment of about 1.3 million video game machines was prohibited temporarily), hazardous substances attracted much attention in various fields and various counter-measures were sought. Prior to the RoHS Directive, EU enforced a directive concerning end-of-life vehicles targeting automobiles[2] (ELV Directive), and on March 1, 2007, China enforced the Law of Prevention of Contamination of Electronic Communication Products targeting electronic communication products (Chinese version of RoHS).Regulation of hazardous substances included in products has been spreading in various fields.

In the summer of 2002, a big consumer-electrics maker requested that HORIBA also perform a rapid screening of trace hazardous elements in electrical and electronic equipment using an X-ray fluorescence analyzer. Therefore, we started to develop the XGT-1000WR and 5000WR series for analysis of hazardous elements in small parts such as electronic parts.Despite the fact that the RoHS Directive has already been enforced, many undecided or obscure points remain unsolved.Therefore, in order to cope with the directive, understanding of not only the function of an analytical apparatus corresponding to the directive but also regulation contents and compliance methods have become important.For the purpose of solving these problems, HORIBA Application Center has introduced not only analytical techniques but also an interpretation of the regulation contents, and the concept behind the compliance methods, etc., by holding seminars and providing training for the use of such apparatus.

In this article, the author will give an outline of the RoHS Directive and the analytical methods of hazardous substances in products and related problems, which have already been introduced in seminars, etc. to users, and further, introduce actual examples of screening analysis using XGT.

Outline of RoHS Directive

The RoHS Directive restricts the use of hazardous substances in electrical and electronic equipment, and prohibits the use of lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyl (PBB) and polybrominated diphenyl ether (PBDE), as a rule. Restricted hazardous substances and the maximum permissible level of each substance according to the RoHS Directive are shown in Table 1.The maximum permissible levels are shown in mass %.When the content is defined as mass %, "rate to what part?", in other words, the denominator in obtaining relative content is important. According to the RoHS Directive, that is defined as "the content per homogenous material".Although there is no detailed definition of homogenous material in the RoHS Directive, in FAQ Document[3] on the RoHS Directive issued by the European Commission, homogenous materials are defined as follows:

(1) 'Homogeneous material' means a material that cannot be mechanically disjointed into different materials.
(2) Homogeneity means completely homogenous state in composition.
(3) 'Mechanically broken down' means separating by mechanical action, e.g. unscrewing, shredding, cutting, crushing, grinding and abrasion.

Table 1 Restricted substances and maximum permissible levels in RoHS Directive

Substance	Maximum permissible level (mass %)
Lead (Pb)	0.1
Mercury (Hg)	0.1
Cadmium (Cd)	0.01
Hexavalent chromium (Cr^{6+})	0.1
Polybrominated biphenyls (PBB)	0.1
Polybrominated diphenyl ethers (PBDE)	0.1

In addition, examples of homogenous materials are described in further detail in a FAQ document, as shown below:

(1) A plastic cover is a 'homogeneous material' if it consists of one type of plastic that is not coated with or has attached to it or inside it any other kinds of materials. In this case, the limit values of the Directive would apply to the plastic.
(2) An electric cable that consists of metal wires surrounded by non-metallic insulation materials is an example of a "non-homogeneous material" because the different materials could be separated by mechanical processes. In this case the limit values of the Directive would apply to each of the separated materials individually.
(3) A semi-conductor package contains many homogeneous materials, which include: plastic molding material, tin electroplating coatings on the lead frame, the lead frame alloy and the gold bonding wires

Examples of homogenous materials are shown in Figure 1 With reference to these examples, you can understand that the RoHS Directive requires considerably detailed confirmation of contents.

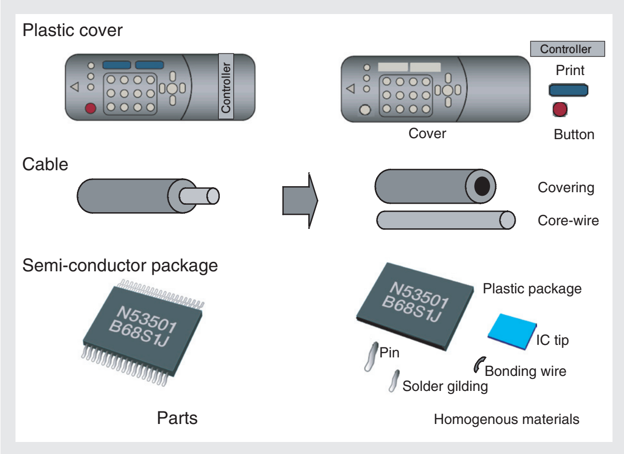

Figure 1 Examples of homogenous materials

Analytical Methods for Hazardous Substances included in Products and Related Problems

To deal with the RoHS Directive, the manufacturers should survey whether any restricted substances are included in the product, confirm compliance of the product to be marketed in the EU with the directive by themselves, and make a self declaration.

The control of hazardous substances included in products is generally performed on the following items, often in combination.

(1) Design step: confirmation of the absence at the time of acceptance of parts by survey and analysis
(2) Procurement step: acquisition of certificate confirming the absence and analytical results from suppliers, and confirmation by analysis of delivered parts
(3) Manufacturing step: process control for prevention of contamination

Many makers not only perform document survey but also require suppliers to submit analytical results, or conduct confirmation by analysis at the time of delivery. This is because parts and materials for which survey on paper showed an absence of hazardous substances have been found to contain restricted substances in many cases.

Concerning the analytical methods, IEC (International Electrotechnical Commission) TC111 (consideration of environment) WG3 (measuring method of chemical substances in products, WG) is now preparing "IEC62321: Procedure for the determination of hazardous substances in electrical and electronic equipment [4]". A characteristic of these standard is to improve analytical efficiency by introducing X-ray fluorescence analysis (XRF) to the screening analysis.

Table 2 Main analytical methods under investigation for IEC62321

Substance	Screening analysis	Details of analysis		
		Plastic	Metal	Electronic part
Cadmium (Cd)	X-ray fluorescence analysis (XRF)	Inductively coupled plasma optical emission spectrometry (ICP-OES) Inductively coupled plasma mass spectrometry (ICP-MS) Atomic absorption spectrometry (AAS)		
Lead (Pb)				
Mercury (Hg)		Inductively coupled plasma optical emission spectrometry (ICP-OES), Inductively coupled plasma mass spectrometry (ICP-MS), Cold vapor atomic absorption spectrometry (CV-AAS), Atomic fluorescence spectrometry (AFS)		
Hexavalent chromium (Cr^{6+})	X-ray fluorescence analysis (XRF) *1	Alkali degradation / colorimetry	Hot water extraction method Spot test method	Alkali degradation / colorimetry
Polybrominated biphenyls (PBB)	X-ray fluorescence analysis (XRF) *2	Gas chromatography – mass spectrometry (GC-MS)	Not applied	Gas chromatography – mass spectrometry (GC-MS)
Polybrominated diphenyl ethers (PBDE)				

*1: By X-ray fluorescence analysis (XRF), only total chromium (Cr) can be analyzed.
*2: By X-ray fluorescence analysis (XRF), only total bromine (Br) can be analyzed.

The main analytical methods under investigation for IEC62321 are shown in Table 2.

Concerning the compliance procedure, the UK Department of Trade and Industry (DTI) issued “RoHS Enforcement Guidance Document Version 1” [5] in May 2006. In this document, DTI states that compliance with the RoHS Directive will be dealt with on the basis of “Presumption of Conformity”. The manufactures should prepare evidence such as a certificate indicating the absence of hazardous substances and analytical results in case of requirement by the executive authorities.

Furthermore, as the method of sampling, the following procedure was proposed.

(1) Narrowing down to samples of materials and applications that are known as “high-risk”.

(2) Narrowing down to samples of materials that can be separated from equipment using routine tools

(3) For components and parts that consist of many kinds of homogenous materials and are mechanically inseparable, and for homogenous materials whose individual analysis is impossible, the homogenization technique is to be used.

As to (3), a question arise as to “for what size part may the homogenization technique be applied? ” The Guidance Document states that “method (3) may be applied to small parts such as tip condensers” and “complete products such as televisions, cellular phones and washing machines, and high density printed PCBs and cables (wire harness) as completed products are not considered to be homogenous materials”. In the business standard of the RoHS Chinese version “Technique required to restrict hazardous substances in electronic communication products (SJ/T 11363-2006)”, it is stipulated that the technique in (3) may be applied to a part smaller than 4 mm^3.

At any rate, when the executive authorities demand, or when some kind of problems on a marketed product are suspected, it is necessary to immediately submit a technical document indicating the conformity of the concerned product with the directive to the executive authorities. In order to satisfy such a requirement, it is important to establish a system for managing the supply chain, and to keep survey information of environmental load substances in the design step and confirmation information at the procurement step as evidence.In the field of electrical and electronic equipment, the survey-answer tool prepared by the Japan Green Procurement Survey Standardization Initiative (JGPSSI) is used, and in the field of automobile, a general data sheets stipulated by the Japan Automobile Manufacturers Association, Inc. (JAMA) and International Material Data System (IMDS; system for collection of information about hazardous substances) are used as data base for the control of hazardous substances.

Actual Screening Analysis

In screening analysis of hazardous elements included in products, handy type XRF, desktop popular type XRF and desktop microscope type XRF are used. The desktop popular type XGT-1000WR series and desktop microscope type XGT-5000WR series are used in the line up at HORIBA.

XGT-1000WR

XGT-1000WR is mainly used at receiving sites where analysis of many parts is required in a short time. The external appearance of XGT-1000WR is shown in Figure 2, and the structure of the measuring part is shown in Figure 3. XGT-1000WR is equipped with a XGT (X-ray Guide Tube: X-ray condensing probe) of 1.2 mm in diameter. After setting an analytical site even for a micro electronic part, the presence or absence of hazardous substances can be determined in a few minutes.

Figure 2 External appearance of XGT-1000WR

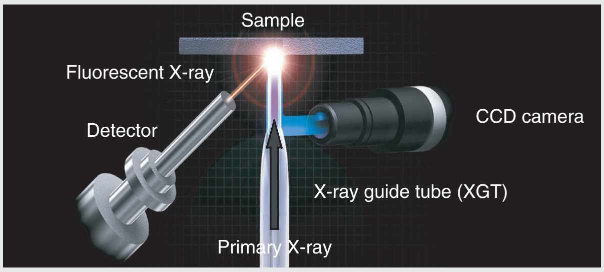

Figure 3 Internal structure of measuring portion

In Figure 4, an example of measurement is shown for a vinyl tie (wired uniting band). As a result, three kinds of ties were separated into “a tie containing lead at more than the maximum permissible level”, “a tie containing trace lead” and “a tie that does not contain any hazardous substance”. External appearance of these ties was entirely indistinguishable, and the presence or absence of any hazardous substances could only be confirmed by measuring. Plastics such as a vinyl tie frequently contain cadmium and lead as paint and stabilizer, and are high-risk materials for which control is difficult.

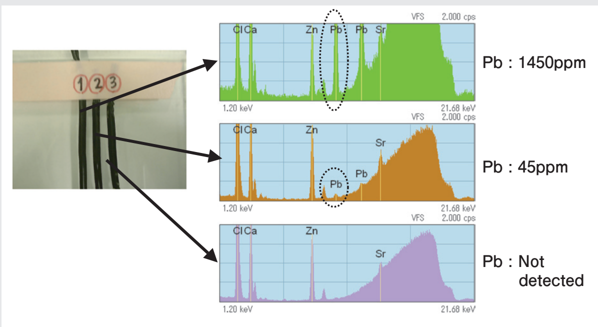

Figure 4 Example of analysis of vinyl ties

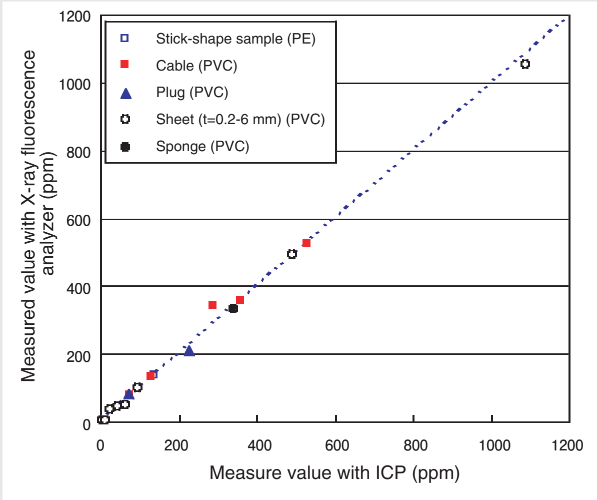

Figure 5 Correlation with ICP in plastic samples

In Figure 5, correlation in the results of analysis of various plastic samples between fluorescent X-ray and ICP is shown[6].

XGT-5000WR

Next, microscope type XGT-5000WR is shown. External appearance of XGT-5000WR is shown in Figure 6 and the conceptual mapping diagram is shown in Figure 7.

Figure 6 External appearance of XGT-5000WR

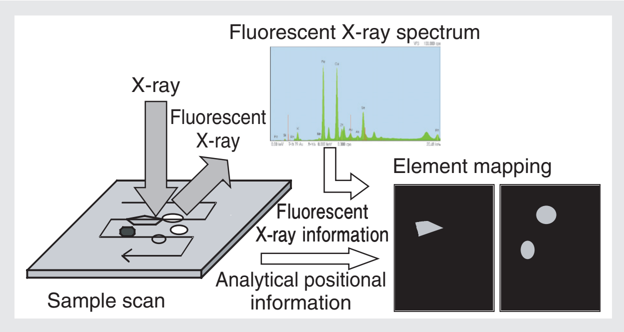

Figure 7 Conceptual mapping diagram analysis

With XGT-5000WR, in addition to point analysis introduced for 1000WR, analysis on a plane called element mapping can be performed. Mapping refers the function that allows us to see distribution of elements as an image. Examples of analysis of AC cords are shown in Figure 8. In AC cord mapping, three kinds of AC cords are appear to contain hazardous substance (Pb) in different regions. Concerning these parts, when the measuring site is wrong, the chance of overlooking the occurrence of a hazardous substance will be high (for example, if only the cable region of the AC cord on the left end is subjected to point analysis, the hazardous substance can not be detected).Therefore, by using the mapping function, the risk of overlooking can be reduced at the time of analysis.

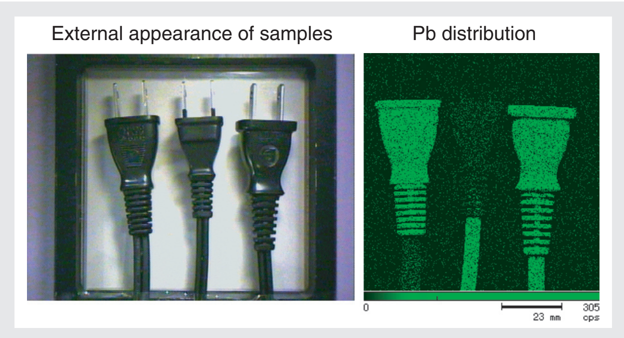

Figure 8 Example of analysis of AC cords (Pb distribution)

In addition, in the case of parts with a high level of integration such as printed-PCBs, the number of mixing of parts containing hazardous substances is high. Example of analysis of a printed-PCB for television (32 cm long × 20 cm wide) is shown in Figure 9. The analyzed PCB was delivered by the supplier as a material conforming to the RoHS Directive. For confirmation of the absence of flaw in this PCB, mapping was performed.As a result, Pb was detected at the two ends of the leading line (manually soldered sites) of Sample 5-4 and at the IC pin region of Sample 5-6. These results indicated that the action of the supplier manufacturing the PCBs to production of Pb-free material was not complete, and possibility of contamination of conventional products was left in the manual soldering process and control of parts.Using the mapping function, it is possible to understand problems in the manufacturing processes that are difficult to find by point analysis, and also become aware of the

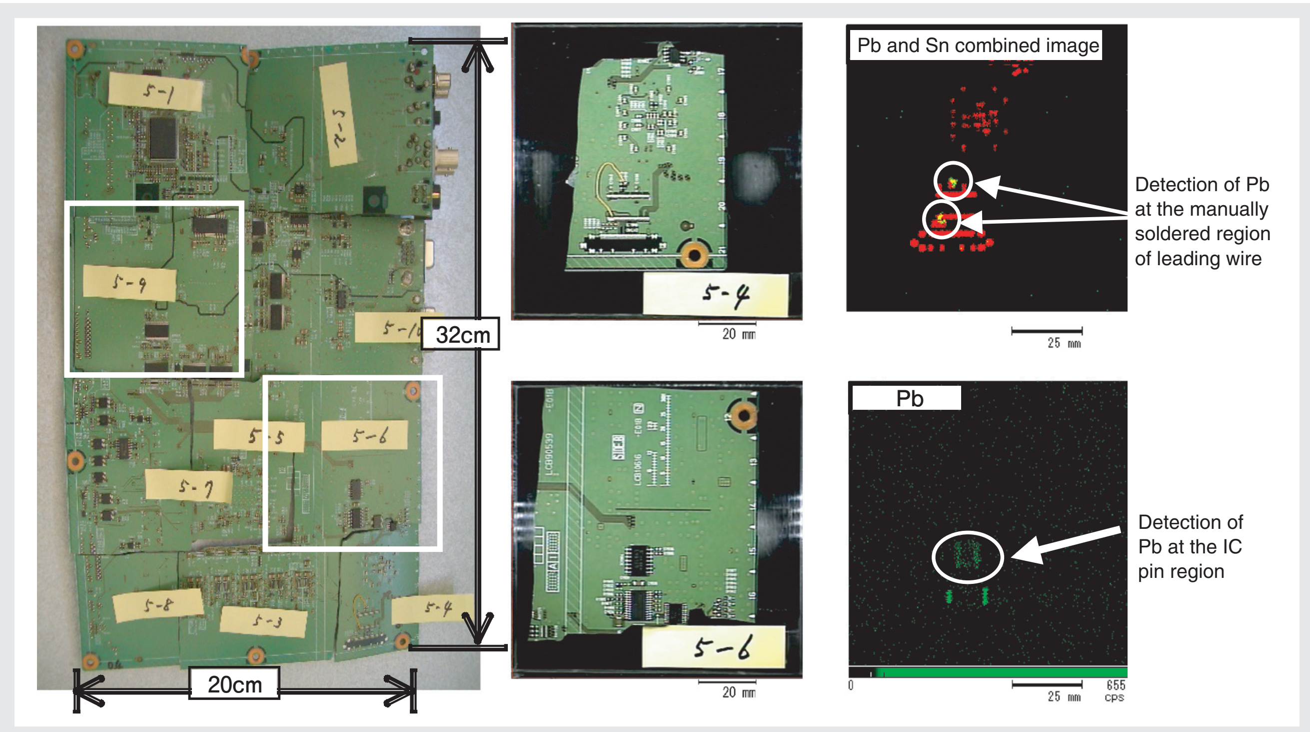

Figure 9 Analysis of printed-PCBs for television

consciousness level of the supplier. Since the PCB examined this time was large, it was divided into 10 cm squares for mapping. However, when using a model with a large sample room, a sample of 20 cm long × 20 cm wide can be analyzed at one time.

Conclusion

In the RoHS Directive enforced by the EU, many points remain obscure in the technical requirements.Under such circumstances, in supplying analytical equipment (XRF) for the purpose of dealing with the Directive, HORIBA Application Center has been aiming not only to supply analytical techniques but also to provide solutions such as interpretation of regulations and compliance methods.

Restriction of the use of hazardous substances is spreading to countries outside the EU. The importance of reduction of hazardous substances included in products is likely to increase further in the future. We will make an effort to provide analytical techniques and information required by users appropriately.

Now, many Japanese manufacturers are dealing with this problem but experiencing great difficulty. However, we believe these efforts will become advantageous for environmental technology in the future.

Reference

[1] Directive 2002/95/EC of the European Parliament and of the Council of 27 January 2003 on the restriction of the use of certain hazardous substances in electrical and electronic equipment, EUROPEAN COMMISSION.

[2] Directive 2000/53/EC of the European Parliament and of the Council of 18 September 2000 on end-of-life vehicles, EUROPEAN COMMISSION.

[3] Frequently Asked Questions on Directive 2002/95/EC on the Restriction of the Use of certain Hazardous Substances in Electrical and Electronic Equipment (RoHS) and Directive 2002/96/EC on Waste Electrical and Electronic Equipment (WEEE); Last updated August 2006, p16-p17, EUROPEAN COMMISSION.

[4] IEC 62321 Ed1/CDV; Procedures for the Determination of Levels of Six Regulated Substances (Lead, Mercury, cadmium, Hexavalent Chromium, Polybrominated Biphenyls, Polybrominated Diphenyl Ethers) in Electrotechnical Products, May 2006, TEC TC111 WG3.

[5] RoHS Enforcement Guidance Document Version 1 issued May 2006, EU RoHS Enforcement Authorities Informal Network.

[6] Sumito Ohzawa, X-ray fluorescence analyzer for hazardous elements corresponding to WEEE/RoHS Directive.*Plastics*, 54(11), 45-50 (2003).

Atushi Bando

Application Center

Manager