

RoHS/ELV Directives - Measurement of Heavy Metals Using ICP-MS

Application

Environmental

Authors

Taichi Yamamoto, Yuki Arai, Tomohiro Seki
Nihon Environmental Services Co., Ltd.
Tokyo
Japan

Abstract

This application note describes a robust analytical method for the determination of heavy metals and substances regulated by the EU Restriction of Hazardous Substances/End of Life Vehicles (RoHS/ELV) directives. Based on the experience of Nihon Environmental Services Co., Ltd in Japan using an Agilent Technologies 7500c ORS (Octopole Reaction System) collision/reaction cell ICP-MS, this note summarizes:

- **An overview and validation of ICP-MS methodology for RoHS applications**
- **Benefits of ICP-MS methodology to the analysis of trace elements in high matrix samples and limitations of EDXRF (Energy Dispersive X-Ray Fluorescence) for the measurement of lead in flame resistant plastics**
- **Advantages of ICP-MS for RoHS applications.**

Introduction

The European Union (EU) RoHS directive (Restriction of the use of certain Hazardous Substances, Directive 2002/95/EC effective July 2006) aims at

effectively eliminating the use of hazardous chemical materials used in electric/electronic products. The EU End of Life Vehicles (ELV) Directive 2000/53/EC covers the use of certain substances in the manufacture of new vehicles and automotive components. In China and Japan, the respective equivalents of the RoHS directive will be enforced at the same time as in the EU. The Japanese version is currently being prepared by the Ministry of Economy, Trade and Industry.

Table 1 shows the substances/metals that are regulated by the RoHS/ELV directives along with their thresholds. The RoHS directive restricts the use of three heavy metals: cadmium (Cd), lead (Pb), mercury (Hg), plus hexavalent chromium (Cr⁶⁺) and two brominated flame retardants. The ELV directive only targets the metals stated above. In accordance with these directives, careful control is required during the manufacture of sub components to prevent the above substances entering into the process. Polymeric resin materials are particularly susceptible to contamination. Nevertheless, other than British Standard/European Standard BS EN1122:2001: Plastics – Determination of Cadmium - Wet Decomposition Method [1], a standard method for analyzing metal impurities in resins does not exist. A National Standardization Technical Committee (TC111) working group 3 organized in the International Electrotechnical Commission (IEC) was set the task of developing standard RoHS analysis methods.



Agilent Technologies

Table 1. Substances Restricted by the RoHS/ELV Directives and Their Thresholds

Restricted substance	RoHS directive/ mg/kg	ELV directive/ mg/kg
Cd	100	100
Pb	1000	1000
Hg	1000	1000
Cr ⁶⁺	1000	1000
PBBs*	1000	—
PBDEs**	1000	—

* Polybrominated biphenyls

** Polybrominated diphenyl ethers

Methodology

Table 2 summarizes the methods of analysis that are performed at Nihon Environmental Services, along with the minimum quantitative detection limits. Official analysis methods for hexavalent chromium include EPA3060A/7196A, (alkaline digestion of hexavalent chromium, colorimetric method), plus JIS H 8625 (hexavalent chromium by a diphenylcarbazine colorimetric method), ISO3856/5 (determination of hexavalent chromium content of the pigment portion of liquid paint or paint in powder form, diphenylcarbazine spectrophotometric method) and DIN53314

(determination of content of chromium (VI) in leather by colorimetric analyses using diphenyl carbazine). None of these, however, have been sufficiently validated for a wide variety of materials. For this reason, it has become general practice at Nihon Environmental Services to measure the total concentration first, and then measure the concentration of the hexavalent form only if the total concentration exceeds the Cr⁶⁺ minimum quantitation limit. Nihon Environmental Services uses US EPA SW-846 Method 3052 (microwave assisted acid digestion of siliceous and organically based matrices, hereafter “EPA3052”) [2]. This screening method specifies the simultaneous pre-treatment procedures for cadmium, lead, mercury, and total chromium.

Nihon Environmental Services Co., Ltd uses an Agilent 7500c equipped with an ORS collision/reaction cell to analyze cadmium, lead and chromium, see Table 3 for operating conditions. Quantitative determination of mercury is also possible provided that the memory effect (the element’s adsorption to the container) and the volatility of the material are taken into account. The instrument was calibrated using a mixed standard solution (SPEX, Metuchen NJ, USA). Table 4 shows the analytical isotopes and internal standards monitored.

Table 2. Minimum Quantitative Detection Limits and Methods of Analysis

Restricted substance	Minimum Level of Quantitation mg/kg	Analysis method	
		Sample preparation	Quantitative Analysis (Technique)
Cd	1	In accordance with the US EPA SW-846 Method 3052 Acid decomposition method with microwave oven	ICP-MS method, see Table 3 for operating parameters
Pb	10		
Hg	1		
Cr	1		
Cr ⁶⁺	10	In accordance with the US EPA SW-846 Method 3060A Hot alkali extraction method	In accordance with the US EPA SW-846 Method 7196A, using Diphenylcarbazine absorption spectroscopy
PBBs	10	Solvent extraction method	GC/MS
PBDE	10	Solvent extraction method	GC/MS

Table 3. ICP-MS Operating Parameters, Agilent 7500c ICP-MS

Nebulizer type	Babington
RF power	1600 W
Sampling depth	8.5 mm
Carrier gas flow rate	1.2 L/min
Makeup gas flow rate	0 L/min
Spray chamber temp	2 °C
Peristaltic pump speed	0.1 rps
Reaction gas	H ₂ (3.5 mL/min)

Table 4. Isotopes Used for Measurements by ICP-MS

Measured element	<i>m/z</i>	Internal Standard (<i>m/z</i>)
Cr	52 53*	Ga (71,69) or Y (89)
Cd	106 111* 112	In (115*) or Y (89) or Te (125)
Hg	200 202*	Tl (205)
Pb	207 208*	Tl (205)

* Isotope that is used primarily for quantitative determination.

Validation of Methodology

Analysis of Standard Reference Materials

A standard polyethylene substance CBR-680 supplied by the Community Bureau of Reference (CBR) was prepared for analysis by ICP-MS according to the procedures detailed in methods EN1122 and EPA3052. The certified value for cadmium in the standard is 140.8 mg/kg. The measured values were subjected to Grubbs' test for outliers to confirm that no samples were to be

rejected. The results were then tested at the 5% significance level to check if there was a difference between the averages calculated by the two methods. The average resulting from the EN1122 method was 143.2 mg/kg (CV: 3.2%, recovery: 101%) and the average from the EPA3052 method was 138.0 mg/kg (CV: 2.4%, recovery 98%). No significant difference was observed between the results.

Results of a Proficiency Test

To test the validity of their ICP-MS methodology the lab took part in the proficiency test in 2004 (IIS04P02): "Cadmium and Lead in Plastics" that was administered by the Institute for Interlaboratory Studies (IIS), in the Netherlands. At present, this is the only international proficiency test that is based on the ISO/IEC Guide 43. According to the report, this test attracted the participation of 56 analytical institutions from 20 countries around the world, with a large number of participants from Japan, Hong Kong, China and other areas in Asia [3]. Three participating labs used ICP-MS, 17 used atomic absorption spectroscopy and 33 used ICP-OES.

Three samples were used in the test. Cadmium was the target metal for #0454 and #0455, while lead was the target for #0456. All samples were polyvinyl chloride (PVC) moldings. Samples #0454 and #0456 contained over 10 times the regulated value of Cd and Pb respectively, while Sample #455 had only a moderate concentration of Cd. The results that Nihon Environmental Services obtained were close to the average for both the EN1122 and EPA Method 3052, as shown in the example histograms for Cd and Pb in Figures 1 and 2. The calculated z-scores were within a range of ± 1 .

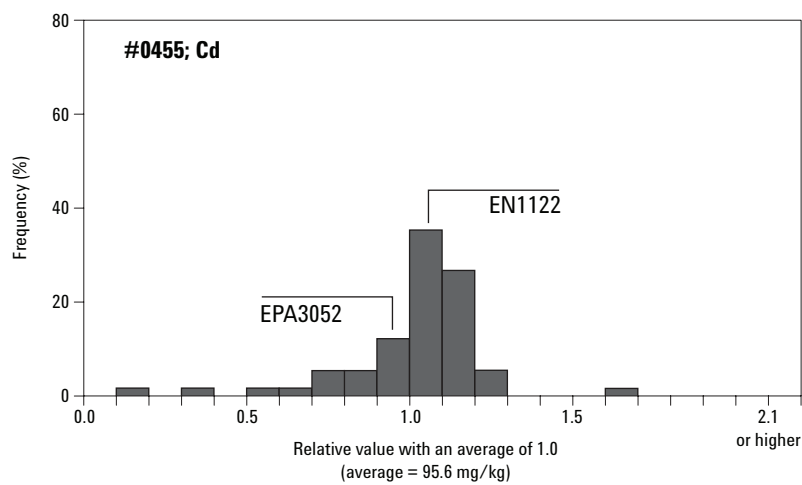
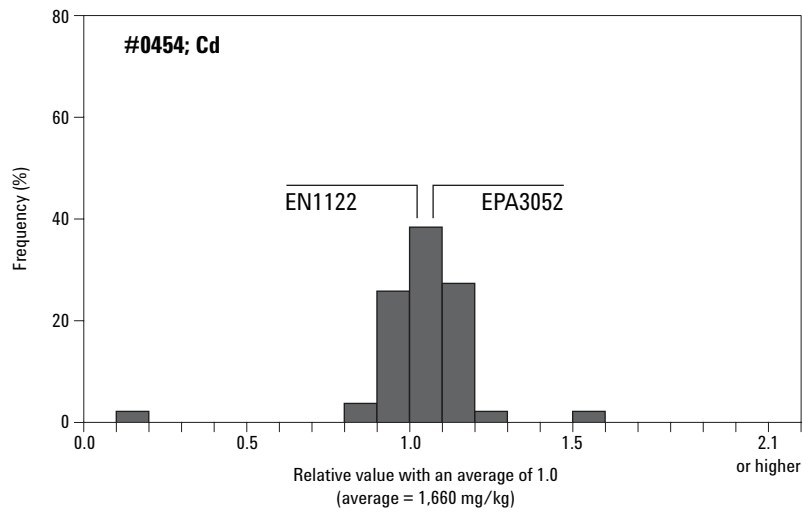


Figure 1. Histograms of results for Cd in sample #0454 and #0455.

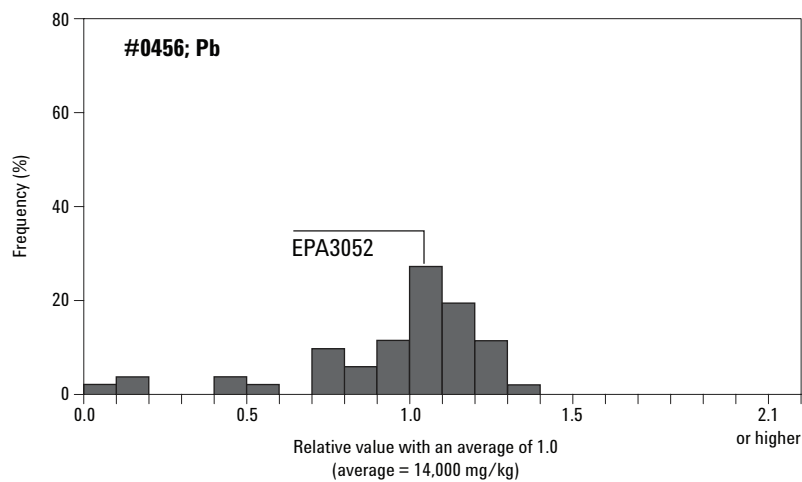


Figure 2. Histogram of results for Pb in sample #0456.

High-Concentration Matrix Samples

The materials covered by the RoHS/ELV directives include various metals and ceramics, as well as polymers. Some resin products contain a large amount of inorganic components as a result of additives such as metal fillers. While resins and other organic components can be decomposed using microwave digestion, their inorganic constituents often remain in high concentrations. It is difficult for some types of analytical instrumentation to measure trace elements in the presence of such high concentration matrices. To overcome this problem, pretreatment methods such as solvent extraction and ion exchange are proposed. Nihon Environmental Services, however, prefers direct quantitative determination and uses ICP-MS with minimum sample pretreatment. By making use of the relative freedom from spectral interferences provided by the 7500c ICP-MS, complicated sample pretreatment procedures are simplified, and the risk of introducing contaminants is minimized. Turnaround time is also improved.

Managing Interferences in ICP-MS

Spectral interferences caused by overlaps of poly-atomic species on elements of interest (cadmium, lead, chromium, and mercury) were overcome by operating the 7500c ORS collision/reaction cell in helium mode (4.5 mL/min flow rate). Physical interferences were corrected through the use of appropriately selected internal standards. Internal standards were selected with similar ionization potential and a similar mass-to-charge ratio to the analytes being measured. Note that the internal standards recommended by the USEPA are not always the most suitable for all matrices.

Limitations of EDXRF for Measurement of Lead in Flame Resistant Plastics

EDXRF spectroscopy can provide quick, low cost analyses. For this reason, this instrument is widely used for screening tests in the electronic, electric appliance and automobile industries, where the number of parts and components used extends from several hundreds to several tens of thousands. Modern EDXRF instruments have improved significantly in sensitivity and are currently capable of measuring at ppm levels under optimized conditions. However, their application is limited because of interferences on key analytes.

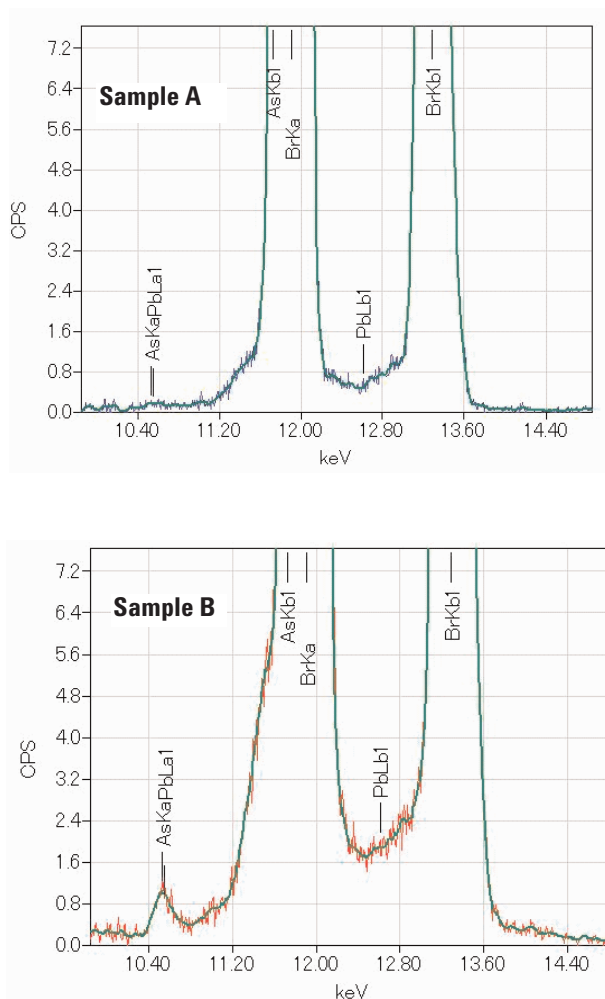


Figure 3. EDXRF spectra of brominated flame retardant containing plastics A (top) and B (bottom).

Figure 3 shows an example of the measurement of lead contained in two flame resistant plastic samples (A and B) using an EDXRF spectrometer. The presence of the prominent peaks associated with bromine suggests that both samples A and B contain brominated flame retardants. EDXRF results also showed less than 10 mg/kg of lead for sample A and 70 mg/kg of lead for sample B. However, analysis by ICP-MS showed less than 10 mg/kg for both samples. The difference in the results for lead in Sample B can be accounted for as follows: Table 5 shows how the wavelength of the lead peak $L_{\alpha 1}$ is close to K_{α} of arsenic, and the $L_{\beta 1}$ and $L_{\beta 2}$ of lead are close to K_{α} and $K_{\beta 1}$ of bromine. This means that it is difficult to determine lead in a sample

which contains arsenic and bromine. Brominated compounds are generally added as a flame retardant and antimony trioxide (SbO_3) is sometimes used to enhance performance. Arsenic compounds are not intentionally added to plastics, however it can occur as a contaminant in the antimony compound. The ICP-MS results for Sample B showed arsenic was present at the 50-ppm level. The comparison demonstrates that ICP-MS provides more reliable results for the determination of heavy metals and other elements such as arsenic, in flame-resistant materials.

Table 5. EDXRF Wavelengths for Quantitative Analysis and Interference Identification

Elements	Spectrum	keV
Pb	$L_{\alpha 1}$	10.552
	$L_{\beta 1}$	12.614
	$L_{\beta 2}$	12.623
As	K_{α}	10.532
	$K_{\beta 1}$	11.727
Br	K_{α}	11.909
	$K_{\beta 1}$	13.292

Advantages of ICP-MS

A major advantage of ICP-MS for RoHS applications is its multi-element capability which enables it to determine a full suite of elements including mercury. This eliminates the need for a peripheral technique such as cold vapor atomic absorption (CVAA) for ICP-optical emission spectroscopy (OES). Antimony (Sb) and arsenic (As) are not currently listed in RoHS/ELV, but these elements are listed along with beryllium (Be) and selenium (Se) in the Green Procurement Guidelines issued by JIG (Joint Industry Guideline) [4] prepared jointly by the industry groups in Japan, the United States and the EU. ICP-MS allows the determination and quantification of all elements specified in current directives and guidelines as well as impurity elements which provide valuable information on the content of the sample.

Another advantage of the technique is its sensitivity. The RoHS/ELV maximum allowable concentration is 100 ppm (Cd) and 1000 ppm (Pb, Cr, Hg). Some manufacturers set specific requirements at, for example, 1/100 or 1/1000 of the RoHS/WEE

threshold which requires determination at lower than the 1–10 ppm level. Because ICP-MS is significantly more sensitive than ICP-OES or AAS, only 1/10–1/100 of the sample amount is required for ICP-MS. This reduces the time required for sample preparation and allows small sample volumes to be analyzed. This is an advantage if the sample itself is very small or the sample is a high value part, such as a noble metal. Further benefits of the simplified sample preparation procedure arise from the reduced volume of acid that is required to digest the sample and that needs to be disposed of at the end of the analysis.

ICP-MS also provides the possibility of employing isotope dilution mass spectrometry (IDMS) as a high caliber reference calibration technique for more accurate quantitative analysis. IDMS involves spiking samples before the dissolution process, which allows accurate calculation of sample preparation recovery.

Conclusions

The ICP-MS method developed at Nihon Environmental Services Co., Ltd. using the 7500c ORS is capable of measuring the four metals regulated by the RoHS/ELV directives efficiently, as well as the 10 heavy metals specified in the guidelines currently prepared jointly by the industries concerned in Japan, the United States and the EU.

To assure the quality of the data acquired according to the RoHS/ELV directives, it is desirable to have reliable third parties perform the same measurements to ensure that the results will be commercially acceptable worldwide. Nihon Environmental Services is ISO9001 accredited and conducts method development according to ISO management. The company also obtained laboratory accreditation (ISO/IEC17025) from the Japan Accreditation Board for Conformity Assessment (JAB) for the measurement of cadmium according to the EN1122 method, which employs ICP-MS as the determination method. IEC TC111 will also include ICP-MS. This experience provides further confidence in the ICP-MS method as applied to the RoHS/ELV directives.

References

1. BSEN1122:2001 “Plastics - Determination of cadmium - Wet decomposition method” (Japanese Standards Association)
2. US EPA SW-846 Method 3052,
<http://www.epa.gov/SW-846/pdfs/3052.pdf>
3. Results Proficiency Test Cadmium and Lead in Plastics October 2004. For more information contact: masahiko_endo@agilent.com
4. Guideline for Standardization of Material Declaration by Japan Electronics and Information Technology Association (JEITA JGPSSI),
<http://home.jeita.or.jp/eps/green2.htm>

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem/icpms.

Agilent shall not be liable for errors contained herein or for incidental or consequential damages in connection with the furnishing, performance, or use of this material.

Information, descriptions, and specifications in this publication are subject to change without notice.

© Agilent Technologies, Inc. 2006

Printed in the USA
January 30, 2006
5989-3574EN



Agilent Technologies