



# Monitoring Heavy Metals by ICP-OES for Compliance with RoHS and WEEE Directives

## Application Note

Inductively Coupled Plasma-Optical Emission Spectrometers

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### Introduction

Manufacturing of electrical and electronic equipment has been a fast developing industry in recent decades. This has resulted in an ever increasing stream of waste electrical and electronic equipment (WEEE) around the world. Over 90% of this waste ends up in landfills. To address the negative impact on the environment and human health caused by the continually increasing volume of WEEE [1,2,3,4], the European Union (EU) has introduced a number of regulations with which manufacturers must comply.

The RoHS (Restriction of Hazardous Substances) Directive 2002/95/EC [5], which will become effective from July 1, 2006, requires the restriction of the use of lead, mercury, cadmium, hexavalent chromium and brominated flame retardants (polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE)) in new electrical and electronic equipment. The upper limits for all substances, except Cd, are 0.1% by weight, or 1000 mg/kg. Cd is limited to 0.01% by weight, or 100 mg/kg.

The WEEE Directive 2002/96/EC [6], which has been effective since August 13, 2005, requires manufacturers to take responsibility for the taking-back, recycling and treatment of virtually all waste electrical and electronic equipment. All equipment subject to that directive will be marked by the crossed-out wheeled bin logo.

The RoHS and WEEE initiatives have now become global. In the US, California has its Electronic Waste Recycling Act of 2003 (SB 20, SB 50) [7], China has drafted RoHS regulations [8,9] and these should be effective in 2006, and Japan has Guidelines for the Management of Chemical Substances in Products [10].



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According to the EU directives, there are ten categories of WEEE:

1. Large household appliances
2. Small household appliances
3. Information technology and telecommunications equipment
4. Consumer equipment
5. Lighting equipment
6. Electrical and electronic tools (with the exception of large-scale stationary and industrial tools)
7. Toys, leisure and sports equipment
8. Medical devices (with the exception of all implanted and infected products)
9. Monitoring and control instruments
10. Automatic dispensers

Of the ten categories listed above, categories 1 to 4 account for almost 95% of the WEEE generated.

To ensure manufacturer/supplier compliance with RoHS and WEEE, there is a need to monitor the restricted chemical substances outlined in the directive. Several analytical instrument techniques can be employed for the determination of these hazardous substances. For example, the heavy metals Cd, Pb, Hg and Cr can be determined by AAS, ICP-OES or ICP-MS [11,12]. Hexavalent chromium can be determined by UV-Vis [13,14], the PPB and PBDE can be determined by GC [15] and GC-MS [16,17]. On the other hand, XRF can also be used for screening heavy metals and total bromine [11,18]. In this article, various sample preparation methods are evaluated for the determination of Cd, Pb, Hg and Cr in plastic by ICP-OES.

## Instrumentation

All measurements were performed on an Agilent 710-ES axial ICP-OES. The instrument includes an echelle polychromator and a megapixel CCD detector providing full wavelength coverage from 177 to 785 nm. The polychromator can be purged with a low flow of either argon or nitrogen for the detection of emission lines of low UV wavelengths.

The standard sample introduction system consists of a glass concentric nebulizer (Conikal) and a glass cyclonic chamber. ICP Expert II software version 1.0 was used for instrument operations. The operating parameters of the system are listed in Table 1.

Table 1. Operating Parameters

Parameter	Instrument operating conditions
Power	1.2 kW
Plasma gas flow	15 L/min
Auxiliary gas flow	1.5 L/min
Nebulizer pressure	250 kPa
Pump rate	15 rpm
Pump tubing	White-white (inlet) Blue-blue (outlet)
Sample uptake rate	1.2 mL/min
Replicate read time	30 s
Background correction	Fitted
Replicate readings	3

A Microwave digestion oven (CEM, Mars 5, ESP 1500 Plus, CEM Corporation, Mathews, NC) was used.

## Materials and Reagents

### Reagents

All chemicals and reagents used were of analytical grade.

- Nitric acid 60%, Analar, BDH
- Hydrochloric acid 32%, Univar, Ajax Finechem
- Sulfuric acid SP Gr. 1.84, Merck
- Hydrogen peroxide 35%, Merck
- Water, distilled deionized, Milli-Q purification system (Millipore)

### Calibration Solutions Preparation

All standards and blank were matrix-matched for the chemicals and reagents used in the sample preparation.

### Certified Reference Materials

Validation of the methods was carried out by using the following certified reference materials:

1. Institute for Reference Materials and Measurements (IRMM)—European Reference Materials ERM-EC 681 Polyethylene [19].
2. National Metrology Institute of Japan (NMIJ)—Certified Reference Material CRM 8102a ABS resin [10].

## Sample Preparation

There is no standard sample preparation method for the determination of heavy metals in plastic, except Method EN 1122 [21] which is only for the determination of Cd in plastic. The use of sulfuric acid in Method 1122 prevents the detection of Pb because of the potential precipitation of  $\text{PbSO}_4$ . On the other hand, EPA Method 3050B [22], which recommends the use of 1–2 g of sample in 10 mL  $\text{HNO}_3$  and heating at 95 °C, is not suitable for the analysis of plastics. Experiments show the 10 mL volume of  $\text{HNO}_3$  is too small, and the heating temperature of 95 °C is not high enough to decompose the plastic material.

EPA Method 3052 [23] recommends microwave digestion with the use of  $\text{HNO}_3$  and HF. Since HF is only required for samples of siliceous matrices, EPA Method 3051A [24] (a microwave digestion method which uses only  $\text{HNO}_3$ ) is adequate. This avoids the hazards associated with the use of HF.

A summary of various sample preparation methods used in this work is listed in Table 2.

Table 2. Digestion Methods

Digestion methods	Analyte(s)
EN 1122 ( $\text{H}_2\text{SO}_4$ – $\text{H}_2\text{O}_2$ )	Cd
$\text{HNO}_3$ – $\text{H}_2\text{O}_2$	Cd, Pb, Cr
EPA 3051A (Microwave digestion with $\text{HNO}_3$ )	Cd, Pb, Cr, Hg

### Method EN 1122 ( $\text{H}_2\text{SO}_4$ – $\text{H}_2\text{O}_2$ Digestion)

Accurately weigh 1 g of sample into a 250 mL beaker, add 10 mL of  $\text{H}_2\text{SO}_4$ , cover with a watch glass, heat on a hot plate at high temperature to decompose and carbonize the organic substances. When white fumes are evolved, continue to heat for about 15 minutes. Remove the beaker from the hot plate and allow to cool for about 10 minutes. Add slowly four 5 mL portions of  $\text{H}_2\text{O}_2$  solution. Allow the reaction to subside after every addition. Heat again for about 10 minutes and allow to cool for 5 minutes. Add a further 5 mL portion of  $\text{H}_2\text{O}_2$  solution and heat again. Stop this procedure when no more organic matter remains. Allow to cool to room temperature and transfer the mixture quantitatively to a 100 mL volumetric flask. Make up the mark with Milli-Q water.

### $\text{HNO}_3$ – $\text{H}_2\text{O}_2$ Digestion

Accurately weigh 1 g of sample into a 250 mL beaker, add 25 mL of  $\text{HNO}_3$ , cover with a watch glass, heat on a hot plate until all dissolved. Cool for 5 minutes, and then add slowly in 1 mL aliquots 10 mL of  $\text{H}_2\text{O}_2$ . Care must be taken to ensure that losses do not occur due to excessive vigorous effervescence. Continue heating the mixture until the volume is reduced to approximately 5 mL. After cooling, transfer the mixture to a 100 mL volumetric flask, and make up to the mark with Milli-Q water. Filter if necessary.

### EPA Method 3051A (Microwave Digestion with $\text{HNO}_3$ )

Accurately weigh 0.5 g of sample into a fluorocarbon microwave vessel equipped with a controlled pressure relief mechanism. Add 10 mL concentrated  $\text{HNO}_3$  to the vessel. Seal the vessel according to the manufacturer's instructions. Properly place the vessel in the microwave system. Digest at 175 °C for 10 minutes. After cooling, carefully uncap and vent each vessel in a fume cupboard. Quantitatively transfer the mixture to a 50 mL volumetric flask, and make up to the mark with Milli-Q water. Filter if necessary.

## Results and Discussion

### Detection Limits

Detection limit is expressed as the concentration giving a net intensity equal to three times the standard deviation of the blank intensity. This was measured at an integration time of 30 seconds and 10 replicates over three separate measurements. The instrument detection limits of Cd, Pb, Cr and Hg are listed in Table 3.

Table 3. Detection Limits

Element	Wavelength (nm)	Detection limit (mg/kg)	RoHS maximum concentration (mg/kg)
Cd	214.439	0.0001	100
Pb	220.353	0.0015	1000
Cr	267.716	0.0002	1000
Hg	194.164	0.0010	1000

## Cadmium

The results of the Cd determination by various digestion methods are listed in Table 4. The measured values are in good agreement with the certified values, except for NMIJ 8102A by Method 1122. Although it is lower, it is consistent with the inter-laboratory value of  $10.3 \pm 0.53$  mg/kg listed in the certificate.

Table 4. Results of the Cd Determination

Digestion method	Cd (mg/kg)			
	EC 681		NMIJ 8102A	
	Measured	Certified	Measured	Certified
EN 1122	$21.5 \pm 0.5$	$21.7 \pm 0.7$	$10.20 \pm 0.20$	$10.77 \pm 0.2$
HNO <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	$21.9 \pm 0.4$	$21.7 \pm 0.7$	$10.70 \pm 0.05$	$10.77 \pm 0.2$
EPA 3051A	$21.7 \pm 0.5$	$21.7 \pm 0.7$	$10.75 \pm 0.16$	$10.77 \pm 0.2$

## Lead

The results of the Pb determination by both HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> and microwave digestion methods are listed in Table 5. For EC 681, the measured values are in good agreement with the certified values. However, for NMIJ 8102a, the measured values are lower than the certified values, but they are consistent with the inter-laboratory value of  $106.6 \pm 5.5$  mg/kg listed in the certificate.

Table 5. Results of the Pb Determination

Digestion method	Pb (mg/kg)			
	EC 681		NMIJ 8102A	
	Measured	Certified	Measured	Certified
HNO <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	$13.7 \pm 0.3$	$13.8 \pm 0.7$	$105.3 \pm 0.3$	$108.9 \pm 0.89$
EPA 3051A	$13.7 \pm 0.4$	$13.8 \pm 0.7$	$106.1 \pm 0.8$	$108.9 \pm 0.89$

## Chromium

The results of the Cr determination by both HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> and microwave digestion methods are listed in Table 6. For EC 681, the measured values are in good agreement with the certified values. However, for NMIJ 8102A, the measured values are lower than the certified values, but they are consistent with the inter-laboratory value of  $26.64 \pm 1.64$  mg/kg listed in the certificate.

Table 6. Results of the Cr Determination

Digestion method	Cr (mg/kg)			
	EC 681		NMIJ 8102A	
	Measured	Certified	Measured	Certified
HNO <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	$17.6 \pm 0.27$	$17.7 \pm 0.7$	$26.9 \pm 0.1$	$27.87 \pm 0.35$
EPA 3051A	$17.5 \pm 0.21$	$17.7 \pm 0.7$	$26.5 \pm 0.4$	$27.87 \pm 0.35$

## Mercury

The results of the Hg determination by both HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> and microwave digestion methods are listed in Table 7. As expected, the open digestion yields low recovery because Hg evaporates during the digestion. Closed vessel microwave digestion is the only method to get complete recovery of Hg.

Table 7. Results of the Hg Determination

Digestion method	Hg (mg/kg)	
	EC 681	
	Measured	Certified
EPA 3051A	$4.60 \pm 0.03$	$4.5 \pm 0.15$
HNO <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	$3.07 \pm 0.49$	$4.5 \pm 0.15$

## Conclusion

The determination of Cd, Pb, Cr and Hg in plastic by ICP-OES has been described. The method EN 1122 (H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>) is only suitable for Cd determination, and the open digestion method with HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> is suitable for Cd, Pb, Cr. However, the microwave digestion method is suitable for Cd, Pb, Cr and Hg. Choosing an appropriate digestion method is essential for good results. The microwave digestion method was shown to be most suitable for the determination of heavy metals in plastic.

In summary, the ICP-OES technique combined with microwave digestion method can be used for routine monitoring of heavy metals in plastic for compliance with RoHS and WEEE regulations.

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