Application Note 43145

Analysis of Trace Elements in Polymer Samples to Ensure Compliance with WEEE-RoHS International Standards using the Thermo Scientific iCAP 7200 ICP-OES

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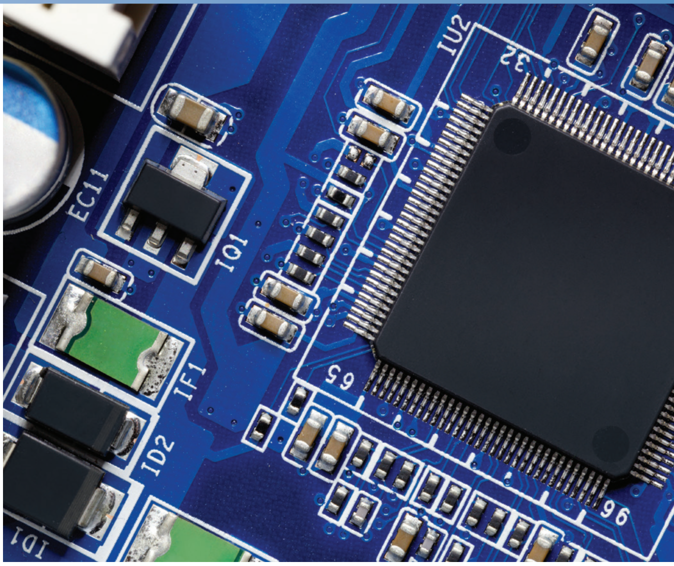

Key Words
IEC 62321, microwave digestion, polymer, trace analysis, waste materials, WEEE/RoHS

Goal

The pre-loaded ICP-OES template ensures optimized sample analysis to enable compliance with WEEE-RoHS and International Electrotechnical Commission protocol IEC 62321 without method development. Additionally the axial plasma viewing enables optimum detection limits for the toxic metals covered by the WEEE-RoHS and IEC regulations. The pre-optimized ICP-OES sample introduction components ensure simple operation and minimal instrumentation and analysis setup time.

Introduction

The Waste Electrical and Electronic Equipment (WEEE) and the Restriction of the use of certain Hazardous Substances (RoHS) Directives of the European Parliament and Council give general guidelines to the member governments on the disposal of WEEE and RoHS in electronic equipment sold in, into and out of the European Union. The directives and legislation affect electronics manufacturers as well as commercial, household equipment producers and consumers. The countries and companies affected are those within the European Union (EU) and in regions that trade with the EU.

The WEEE [1] and RoHS Directives [2] are guidelines set out by the European Parliament detailing the goals for the disposal of waste electronic equipment and the restrictions applied to the sale of new equipment in the EU. Individual member governments must determine how best to implement these guideline directives to achieve the EU goals in their respective countries.

The WEEE Directive specifically targets the responsible recycling of separately collected waste electronic equipment and does not govern the hazardous content of that equipment. The RoHS Directive restricts sales in the EU market of any new electrical or electronic equipment containing more than the agreed levels of hazardous substances and is thus used as a pre-emptive control of waste.

The guidelines and laws enacted by the individual governments also pertain to the importation of goods into the EU and thus affect a great number of countries around the world [3].

The RoHS regulations require analysis of materials used in electronic equipment to restrict and verify the concentrations of cadmium, hexavalent chromium, lead, mercury, polybrominated biphenyl and diphenyl ethers. The maximum limits of hazardous substances are calculated on "homogenous materials" which means a material that cannot be mechanically separated into its component materials. The maximum allowable quantities in electrical equipment of the hazardous substances listed above are:

- 0.1 % by weight for hexavalent chromium, lead, mercury, polybrominated biphenyl and diphenyl ethers
- 0.01 % by weight for cadmium

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International Electrotechnical Commission Analysis Protocol – IEC 62321

The International Electrotechnical Commission (IEC) *"is the leading global organization that publishes consensus-based International Standards and manages conformity assessment systems for electric and electronic products, systems and services, collectively known as electrotechnology"* [4]. The IEC 62321 protocol for the analysis of restricted substances provides guidelines for the sampling and analysis of all the restricted substances in electronics and polymers found in electronic parts or equipment. With regards to the ICP-OES technique, only cadmium, lead and mercury are considered for analysis since chromium requires a separation technique to be used to allow the hexavalent form to be analyzed. However, using ICP-OES instrumentation with simultaneous detection capability allows the analysis of total chromium with no extra cost or time penalty and can provide a valuable screening tool to determine if further chromium speciation analysis is required.

Instrumentation

The Thermo Scientific™ iCAP™ 7200 ICP-OES was used for the analysis of polymer materials which are a common component of materials governed by the RoHS legislation [5]. The iCAP 7200 ICP-OES is a compact dual view ICP-OES instrument that provides powerful analyte detection capabilities within a small footprint to provide a highly cost effective solution for the routine analysis of smaller batches of liquid samples. The instrument software, Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™, incorporates several pre-loaded templates (see Figure 1) which can be employed to enable simple operation with minimal method development. These pre-loaded templates include all measure modes and peak/background positions required to determine the analytes required for compliance with WEEE/RoHS protocols.

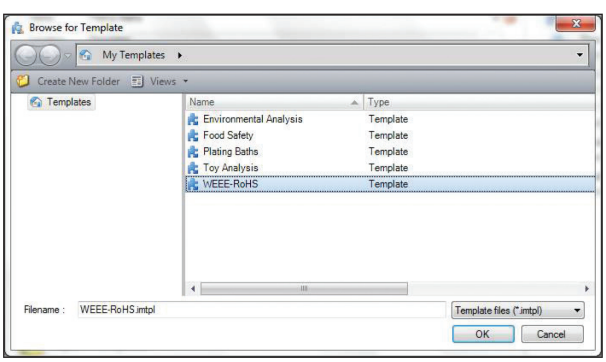

Figure 1. WEEE-RoHS template selection

Sample and Standard Preparation

The Certified Reference Materials (CRMs) chosen to demonstrate analytical performance capabilities were obtained from LGC Limited (UK) and were specifically developed to provide certified standards for the analysis of polymers subject to WEEE-RoHS legislation. The CRMs chosen for this analysis were supplied in small chips and are listed as follows:

- EC680 – polyethylene (low level)
- EC681 – polyethylene (high level)
- PVC2 – polyvinyl chloride
- PVC1 – polyvinyl chloride with low concentrations of analytes, used to determine the method detection limits (MDL)

The range of element concentrations present in the polymers are representative of typical ranges that may be found in manufactured polymers. The samples were digested and processed as supplied, without further grinding or freeze milling.

The IEC 62321 protocol contains sampling recommendations and dissolution guidelines for materials and various samples which require analysis for RoHS hazardous substances including metals, polymers and electronic components. The certified reference polymer chips used in this analysis are expected to be homogenous in terms of their elemental composition. However, this may not always be the case and it is therefore recommended to analyze multiple sample chips from any given sample in order to establish homogeneity.

The sample preparation detailed below is based on one of several methods suggested by the IEC 62321 protocol. In this case, a microwave digestion method was utilized due to the potential volatile nature of the analytes as well as the simplicity of the digestion matrix and speed of dissolution. The coarsely ground CRM samples (which were used as supplied) were also used by the IEC to determine the efficacy of the IEC 62321 method protocol. The sample masses were intentionally kept to a minimum so that any matrix differences between samples and standards are also minimized. This approach was taken to remove the necessity for internal standards, thereby keeping the method simple and easy to implement. The required quantification of 0.01% (0.01µg/mL) for cadmium and 0.1% (0.1µg/mL) for chromium, lead and mercury at this mass and volume is comfortably within the capabilities of the iCAP 7200 ICP-OES.

A mass of approximately 0.1g of each sample was weighed into individual Teflon® microwave digestion vessels and 10mL of analytical grade nitric acid (37% mass by volume) was added to digest the sample. A trace or catalytic quantity (0.1mL or less) of hydrogen peroxide may also be added to aid complete digestion and the vessels were then sealed and the samples digested in the microwave as detailed in Table 1.

Table 1. Microwave digestion parameters

Maximum power (W)	Ramp time to control (mins)	Control (°C)	Hold time (mins)
1600	20	110	20
1600	10	130	10
1600	20	170	20

The digested samples were quantitatively transferred into 100 mL flasks with deionized water and made up to 100 mL in preparation for the analysis by ICP-OES. An aliquot was also decanted from each of the EC680, EC681 and PVC2 samples and spiked with the equivalent of 0.1 µg/mL of all the analytes.

(Note: the PVC1 CRM was used solely to provide a matrix blank for the determination of the method detection limit.)

Method Development

The WEEE-RoHS template was opened in the Qtegra ISDS and contains all of the required method parameters and standard concentrations to verify WEEE-RoHS compliance. A standard sample handling kit was used for the analysis as described in the method notes and the method parameters are shown below in Table 2 for reference.

Table 2. Method parameters

Parameter	Setting
Pump tubing	Sample Tygon® orange/white Drain Tygon® white/white
Pump speed	45 rpm
Nebulizer	Glass concentric
Nebulizer gas flow	0.15 MPa
Spray chamber	Glass cyclonic
Auxiliary gas flow	1.0 L/min
Coolant gas flow	12 L/min
Center tube	2 mm
RF Power	1150 W
Torch Orientation	Duo (axial)
Exposure times	10 sec

The samples and their spikes were analysed in a single run after calibration with a suitable set of standards and the standard concentrations are shown in Table 3 for reference. The standards were prepared by diluting traceable 1000 µg/g aqueous single element standards and the same high-purity nitric acid that was used for the sample dissolution was added to the standards to produce a final set of standards containing 5% nitric acid.

Table 3. Standard concentrations (mg/kg)

Element	Blank	Standard 1	Standard 2	Standard 3
Cd	0	0.1	0.5	1
Cr	0	0.1	0.5	1
Hg	0	0.1	0.5	1
Pb	0	0.1	0.5	1

Results

The analytical results of the polymer sample analysis are shown below in Table 4 and the recoveries are further highlighted in Figure 2. The samples and the spikes were analyzed in the same run. The majority of the spike recoveries readback within a range of ± 10% relative to the accepted values and the spiked concentrations. Two of the analyte results for sample EC681 (Cr and Hg) were within 15% relative to the accepted values and may be attributed to minor inhomogeneities within the digested sample chips. It should also be noted that although the low-level analyte results for EC681 show variation from the accepted value, the spike results are well within expectations.

Method detection limits (MDL) shown in Table 4 were established for the analytes by analyzing the PVC1 polymer CRM using ten replicates measurements and multiplying the standard deviation of the results by 3 to give a 3σ detection limit. PVC1 has minimal or no detectable concentrations of three out of four restricted elements in a typical polymer matrix and is therefore considered to be appropriate for the purpose of MDL calculation. The MDL figures show the low detection limits which typify the powerful performance of the iCAP 7200 ICP-OES.

The sample results and spike recoveries shown in Table 4 demonstrate the sensitivity and accuracy of the iCAP 7200 ICP-OES for WEEE-RoHS applications and the unique pre-loaded method template and pre-optimized sample introduction settings enable powerful analytical performance with little or no requirement for analyst intervention or method development.

Table 4. Results of the analysis of polymer CRMs

Cd 214.438 nm					
CRM	Spike (µg/mL)	µg/g in solid sample	Certified µg/g in solid CRM	% CRM recovery	% Spike recovery
EC680	0.1	144.6	140.8	102.7	102.6
EC681	0.1	22.0	21.7	101.4	103.0
PVC2	0.1	37.0	35.0	105.6	97.6
PVC1 MDL	-	0.09	-	-	-

Cr 267.716 nm				
CRM	µg/g in solid sample	Certified µg/g in solid CRM	% CRM recovery	% Spike recovery
EC680	110.0	114.6	96.0	101.8
EC681	15.3	17.7	86.3	99.4
PVC2	1.7	NA	NA	97.1
PVC1 MDL	0.65	-	-	-

Hg 194.227 nm				
CRM	µg/g in solid sample	Certified µg/g in solid CRM	% CRM recovery	% Spike recovery
EC680	23.3	25.3	92.1	93.5
EC681	4.8	4.5	105.8	114.9
PVC2	<DL	NA	NA	90.6
PVC1 MDL	1.19	-	-	-

Pb 220.353 nm				
CRM	µg/g in solid sample	Certified µg/g in solid CRM	% CRM recovery	% Spike recovery
EC680	106.1	107.6	98.6	100.8
EC681	12.8	13.8	92.5	100.4
PVC2	93.5	89.0	105.0	95.5
PVC1 MDL	1.21	-	-	-

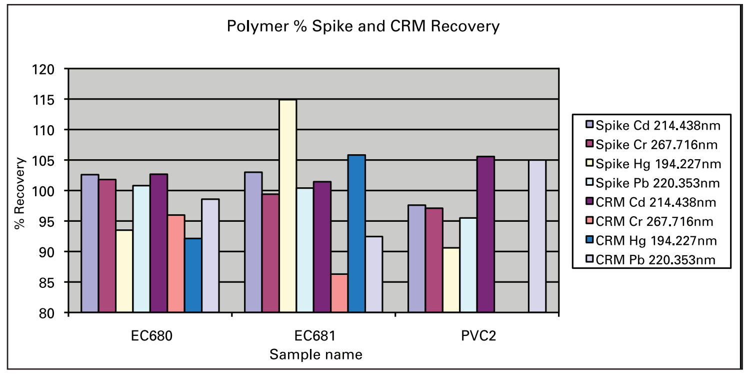

Figure 2. Graphical representation of spikes recovery

Conclusion

The analysis of polymer samples to verify compliance with WEEE-RoHS legislation is highly efficient and cost effective with the Thermo Scientific iCAP 7200 ICP-OES. The Thermo Scientific Qtegra™ Intelligent Scientific Data Solution with preloaded templates and pre-optimized sample introduction components enable even the inexperienced user to significantly reduce the normal method development time needed for typical WEEE-RoHS sample analysis.

References

[1] EU WEEE Directive
http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2012:197:0038:0071:EN:PDF

[2] EU RoHS Directive
http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2011:174:0088:0110:EN:PDF

[3] EU webpage for links to all WEEE-RoHS legislature
http://ec.europa.eu/environment/waste/weee/legis_en.htm

[4] Definition and IEC Standards from the IEC website
http://www.iec.ch/

[5] EU webpage on changes to WEEE-RoHS initiatives
http://ec.europa.eu/environment/waste/weee/index_en.htm

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