

Analysis of trace elements in polymer samples to ensure compliance with WEEE-RoHS standards using the Thermo Scientific iCAP 7200 ICP-OES

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Goal

To demonstrate the ability of the Thermo Scientific iCAP 7000 Plus Series ICP-OES to monitor analytes in electrical and electronic goods for compliance with WEEE/RoHS regulations.

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 WEEE¹ and RoHS Directives² 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 world³.

The RoHS regulations require analysis of materials used in electronic equipment to restrict and verify the concentrations of cadmium, hexavalent chromium, lead, mercury, polybrominated biphenyls, diphenyl ethers, and phthalates. 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 lead, mercury, hexavalent chromium, polybrominated biphenyls, diphenyl ethers and phthalates
- 0.01% by weight for cadmium

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*™”. 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 Duo was used for the analysis of polymer materials which are a common component of materials governed by the RoHS legislation⁵. The iCAP 7200 ICP-OES Duo 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. A standard sample introduction kit, containing a glass concentric nebulizer and a glass cyclonic spray chamber was used.

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% (0.1 g·L⁻¹) for cadmium and 0.1% (1 g·L⁻¹) for lead, mercury, and chromium at this mass and volume is comfortably within the capabilities of the iCAP 7200 ICP-OES Duo.

A mass of approximately 0.1 g of each sample was weighed into individual PTFE microwave digestion vessels and 10 mL of analytical grade nitric acid (37% mass by volume) was added to digest the sample. A trace or catalytic quantity (0.1 mL 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 Figure 1.

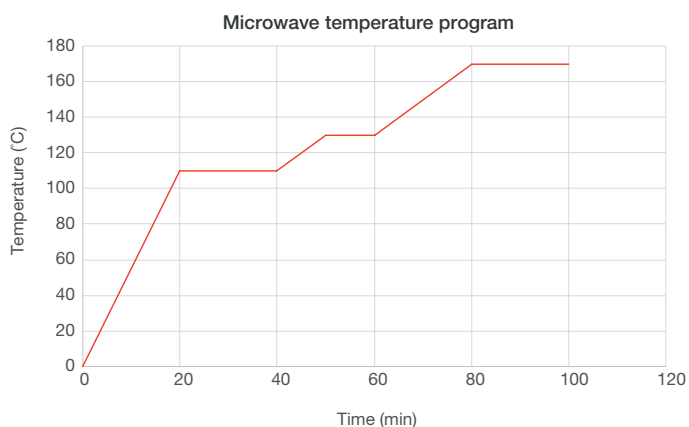


Figure 1. Microwave digestion program.

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 mg·L⁻¹ 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

A LabBook was set up using the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software for the analysis of the elements covered by WEEE-RoHS regulation. Method parameters and sample introduction components are shown in Table 1.

Table 1. Method parameters.

Parameter	Setting
Pump Tubing (Standard Pump)	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 ⁻¹
Coolant Gas Flow	12 L·min ⁻¹
Center Tube	2 mm
RF Power	1150 W
Plasma View	Axial
Exposure Time	UV 10 s, Vis 10 s

The samples and their spikes were analyzed in a single run after calibration with a suitable set of standards and the standard concentrations are shown in Table 2 for reference. The standards were prepared by diluting traceable 1000 mg·kg⁻¹ 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 2. Standard concentrations (mg·kg⁻¹).

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 3 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 read back within a range of $\pm 10\%$ 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 3 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 Duo.

The sample results and spike recoveries shown in Table 3 demonstrate the sensitivity and accuracy of the iCAP 7200 ICP-OES Duo for WEEE-RoHS applications.

Table 3. Results of the analysis of polymer CRMs.

Cd 214.438 nm				
CRM	mg·kg ⁻¹ in solid sample	Certified mg·kg ⁻¹ in solid CRM	CRM recovery (%)	Spike recovery (%)
EC680	144.6	140.8	102.7	102.6
EC681	22.0	21.7	101.4	103.0
PVC2	37.0	35.0	105.6	97.6
PVC1 MDL	0.09	-	-	-

Cr 267.716 nm				
CRM	mg·kg ⁻¹ in solid sample	Certified mg·kg ⁻¹ 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	mg·kg ⁻¹ in solid sample	Certified mg·kg ⁻¹ 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	mg·kg ⁻¹ in solid sample	Certified mg·kg ⁻¹ 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	-	-	-

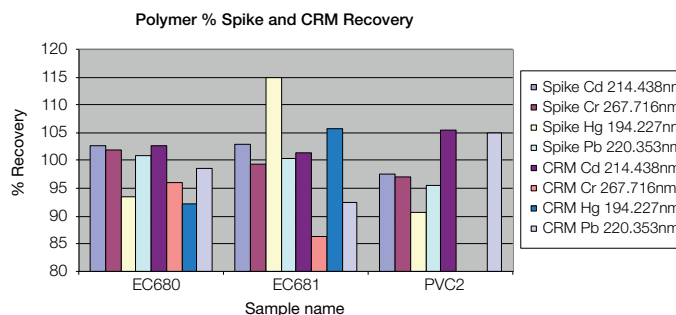


Figure 2. Graphical representation of spikes recovery.

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 Duo. The Thermo Scientific Qtegra ISDS Software allows even for unexperienced users to set up a method in conformity with specific regulations, easy sample analysis and post-acquisition data manipulation.

References

1. EU WEEE Directive <http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32012L0019&from=EN>
2. EU RoHS Directive <http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32011L0065&from=EN> and <http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32015L0863&from=EN>
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

Find out more at thermofisher.com/ICP-OES

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