APPLICATION NOTE

ICP-Optical Emission Spectroscopy

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Meeting the RoHS Directive with Microwave Sample Preparation and the Avio 220 Max ICP-OES

Introduction

With the increasing use of and reliance on electronics, manufacturers are continually developing new products with enhanced capabilities. As a result, the lifetime of electronics is becoming shorter as consumers more frequently upgrade to newer, more advanced models. The result is an increasing number of electronics being disposed. Although electronics recycling programs have been implemented and are growing, the number of electronic products being discarded continues to rise.

Since electronics contain many components, there is a high likelihood that metals will enter the environment after items are discarded. The toxic metals of greatest concern are cadmium (Cd), chromium (Cr, specifically hexavalent Cr [CrVI]), mercury (Hg), and lead (Pb). To address this issue, the Restriction of Hazardous Substances (RoHS) directive[1] implements limits for the levels of Cd, CrVI, Hg, and Pb which can be present in electronic devices, as shown in Table 1.

Table 1. RoHS Elemental Limits.

Element	Limit
Cadmium	0.01%
Chromium (hexavalent)	0.1%
Mercury	0.1%
Lead	0.1%

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The simplest and most efficient way to meet the RoHS directive is to use microwave digestion for sample preparation and inductively coupled plasma optical emission spectroscopy (ICP-OES) for analysis. Although ICP-OES cannot distinguish different forms of elements, total Cr can be measured to determine if it is above or below the regulated level. If above the limit, the samples can be further prepared and analyzed by other techniques to determine CrVI.

This work will focus on the analysis of a variety of sample types present in electronics for compliance with the RoHS directive using ICP-OES, along with sample preparation considerations.

Experimental

Samples and Sample Preparation

Since there are a wide variety of sample types which fall under the RoHS directive, it is impossible to evaluate all of them. Nevertheless, a representative selection of sample types was analyzed: plastics, wire insulation, solder, wire, and a circuit board, all taken from discarded electronic products (with the exception of the solder, which was new). Given the diversity of possible sample types, microwave digestion provides the most flexibility and highest probability of complete digestion. While it is possible to optimize the microwave methodology for each sample type, the goal was to develop a single sample preparation scheme which would be applicable to many sample types in order to simplify the sample preparation process. Although a single method was not possible for this sample set, the preparation variations between sample types were minimized.

Table 2 shows details of the samples evaluated which were collected from discarded electronic equipment (with the exception of the solder, which was purchased new). Each sample was cut into small pieces, and 0.2 g portions were used for analysis.

All samples were digested in a PerkinElmer Titan MPS™ microwave sample preparation system. First, 0.2 g of sample was added to each digestion vessel, followed by the appropriate acids (trace metal grade) as shown in Table 2, with the nitric acid added first to each. The vessels were left open for about 10 minutes to allow for any pre-digestion that may occur before being sealed and placed in the Titan MPS system. Table 3 shows the Titan program used for all samples; only the acids differed between the sample types.

After digestion, the samples were diluted to 50 mL with 5% HCl (v/v) to complex the mercury. The exception was the solder, which was diluted with deionized (DI) water since the HCl caused the formation of a white precipitate. With this sample preparation scheme, the regulatory levels for the elements in solution are shown in Table 4.

All quantitative measurements were made against calibration curves prepared in a mixture of 10% nitric acid (v/v), 5% sulfuric acid (v/v), and 1% hydrochloric acid (v/v) using 0.5 and 1 ppm standards, with yttrium (Y, 0.5 ppm) used as an internal standard. To assess accuracy, pre-digestion spikes at the regulatory levels and 10x below were added to the digestion vessels prior to adding the acids.

Table 2. Sample Information.

Group	Acids Used for Digestion	Sample Type	Specific Sample Info
1	HNO_3 (70%) 6 mL H_2SO_4 (98%) 4 mL	Plastic	Black (from TV remote control) White (from cordless telephone)
		Wire Insulation	Green(from surge protector) Black (from surge protector) White (from surge protector) Tan (from surge protector power cord)
		Metal	Copper wire (from surge protector)
2	HNO_3 (70%) 8 mL HF (49%) 2 mL	Circuit Board	From cordless phone (chips removed)
		Metal	Solder (RoHS compliant)

Table 3. Titan MPS Microwave Digestion Program.

Step	Temp (°C)	Pressure Limit (bar)	Ramp (min)	Hold (min)	Power (%)
1	170	35	5	5	90
2	220	35	5	15	90
3	50	35	1	10	0

Table 4. Regulatory Levels for RoHS Elements in Solution with Current Sample Preparation Procedure.

Element	RoHS Limits (% in solid)	RoHS Limit in Solution (mg/L)
Cadmium	0.01	0.4
Chromium	0.1	4
Lead	0.1	4
Mercury	0.1	4

Instrumental Conditions

All analyses were performed with a PerkinElmer Avio® 220 Max hybrid simultaneous ICP-OES operating in axial mode. The elements and wavelengths are listed in Table 5, and the instrumental parameters appear in Table 6. Yttrium was added to all standards and samples at 0.5 ppm. The rinse solution contained 5% nitric acid (v/v) and 2% hydrochloric acid (v/v), with the HCl being present to aid in mercury washout.

Because the compliance limits for RoHS are at concentrations easily seen with the Avio 220 Max, a short auto integration time window could be used, increasing analytical speed and sample throughput without sacrificing accuracy (Figure 1). With Avio's unique Flat Plate™ plasma technology, all analyses were performed using only 8 L/min of argon. This low flow, combined with rapid sample analysis, minimizes argon consumption and cost.

Table 5. Elements and Wavelengths

Element	Wavelength (nm)
Cadmium	228.802
Chromium	267.716
Lead	220.353
Mercury	253.652
Yttrium (int. std.)	371.029

Table 6. Avio 220 Max ICP-OES Instrumental Parameters

Parameter	Value
Nebulizer	Cross flow
Spray Chamber	Ryton Scott double-pass
Sample Uptake Rate (mL/min)	1.5
Plasma Flow (L/min)	8
Aux Flow (L/min)	0.2
Nebulizer Flow (L/min)	0.6
RF Power (W)	1500
Viewing Distance (mm)	15
View	Axial
Integration Window	0.1-2.0 sec

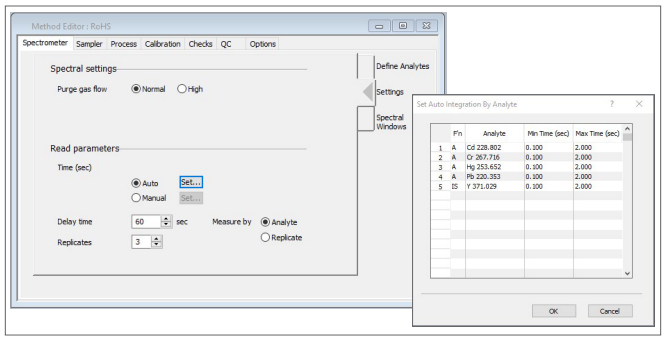

Figure 1. The auto integration capability in Syngistix™ for ICP software automatically determines the most appropriate integration time for each element: the higher-concentration analytes were read with a shorter time, while the lower-concentration ones used a longer integration time.

Results and Discussion

Initially, it is important to establish the digestion conditions. Although the goal of a single acid mixture and single Titan program for all samples in this study was not realized, it was found that two different acid mixtures could be used with the same program to effectively digest all samples. Due to the diverse nature of the samples, sulfuric acid was found to be effective since it significantly lowers the vapor pressure in the vessels, allowing higher temperatures to be attained, thus significantly increasing the efficiency of the nitric acid. However, the sulfuric/nitric acid mixture did not completely dissolve the circuit board or solder, most likely due to presence of silica. As a result, hydrofluoric acid was required and found to be effective when mixed with nitric acid.

In all cases, a significant amount of gas was generated during the digestion. Most of the dissolved gas was expelled during transfer to the autosampler tubes and dilution. However, it is recommended that the samples be allowed to sit in open containers for thirty minutes prior to analysis to completely degas. Dissolved gas present in the samples results in high relative standard deviations during the analysis.

While these conditions were found to be effective for all the samples in this study, it cannot be guaranteed that they will yield complete digestions for all possible sample types covered under the RoHS directive, but can serve as a starting point. Regardless of the required acid combinations, closed vessel digestion must be used to prevent loss of Hg, a volatile element.

To establish the accuracy of the calibration, check standards at ten times less than the RoHS levels (in solution) were analyzed directly after the calibration curves. Table 7 shows the recoveries, which indicate accurate results at both low and high levels.

With the ability to accurately measure both low and high concentrations established, the samples were analyzed; the results are shown in Table 8. For Cd, Cr, and Hg, all samples were below the RoHS limits. However, the Pb levels varied significantly between samples. Both plastics and the copper wire had Pb present below the regulated levels. Although there is Pb present in the solder, it is also below the RoHS level, confirming that the solder is RoHS compliant. However, Pb was above the regulated level in all of the wire insulations and the circuit board; repeated analyses of multiple samples of all the wire insulations and circuit board yielded equivalent result. The high Pb values from the circuit board most likely result from the use of non-RoHS-compliant solder.

Table 7. Recoveries of Low and High Level Check Standards.

Element	Low Standard (ppm)	Recovery (%)	High Standard (ppm)	Recovery (%)
Cd	0.04	101	0.4	97
Cr	0.4	96	4	93
Hg	0.4	99	4	97
Pb	0.4	98	4	96

Table 8. Sample Analysis.

Sample	Cd (weight %)	Cr (weight %)	Hg (weight %)	Pb (weight %)
Plastic (white)	< 0.001	< 0.001	< 0.001	< 0.001
Plastic (black)	< 0.001	< 0.001	< 0.001	0.001
Wire Insulation (green)	< 0.001	0.005	< 0.001	**0.927**
Wire Insulation (black)	0.004	< 0.001	0.001	**1.01**
Wire Insulation (white)	< 0.001	< 0.001	< 0.001	**1.31**
Wire Insulation (tan)	< 0.001	< 0.001	< 0.001	**1.09**
Solder (RoHS compliant)	< 0.001	< 0.001	0.002	0.053
Circuit Board	< 0.001	< 0.001	< 0.001	**0.363**
Copper Wire	< 0.001	< 0.001	0.002	< 0.001

*Results in bold indicate concentrations above the RoHS limits.

To assess the accuracy of the methodology and confirm that the sample preparation process does not affect recoveries, pre-digestion spikes were evaluated. For selected samples, spikes were added to the digestion vessels after the addition of sample, but before the acids were added. Spikes were made at two levels: ten times below and at the RoHS levels (in solution). The Cd was spiked at concentrations ten times lower than the other elements, due to the RoHS regulations being 10x lower for Cd than the other elements. All recoveries are within 10% of the spiked values (as shown in Table 9), indicating that no significant contamination or element loss occurs during the digestion process. The accuracy of the methodology is also validated by the accurate spike recoveries.

Table 9. Pre-digestion Spike Recoveries.

Sample	Spike (ppm)		Cd (% Recovery)	Cr (% Recovery)	Hg (% Recovery)	Pb (% Recovery)
	Cd	Others				
Digest Blank	0.04 0.4	0.4 4	100 97	95 92	100 104	103 105
Plastic – White	0.04 0.4	0.4 4	99 99	96 98	100 104	103 105
Copper Wire	0.04 0.4	0.4 4	108 101	91 90	95 95	104 107

Conclusion

This work has demonstrated the ability of the Titan MPS microwave digestion system and Avio 220 Max hybrid simultaneous ICP-OES to rapidly and accurately measure elements in a variety of sample types which fall under the RoHS directive. With the proper choice of acids, a variety of different sample types can be digested using a single Titan MPS microwave program, minimizing sample preparation complexity for the wide variation of sample types which fall under the RoHS directive. Pre-digestion spike recoveries prove that elements are not lost during the sample preparation procedure and that significant contamination is not introduced.

References

1. http://ec.europa.eu/environment/waste/rohs_eee/index_en.htm

Consumables Used

Avio 220 Max ICP-OES	
Component	**Part Number**
Sample Uptake Tubing – 0.76 mm id (Black/Black) PVC	09908587
Drain Tubing – 1.14 mm id (Red/Red) PVC	09908585
Pure-Grade Cadmium Standard, 1000 mg/L	N9300176 (125 mL) N9300107 (500 mL)
Pure-Grade Chromium Standard, 1000 mg/L	N9300173 (125 mL) N9300112 (500 mL)
Pure-Grade Mercury Standard, 1000 mg/L	N9300174 (125 mL) N9300133 (500 mL)
Pure-Grade Lead Standard, 1000 mg/L	N9300175 (125 mL) N9300128 (500 mL)
Pure-Grade Yttrium Standard, 1000 mg/L	N9303810 (125 mL) N9300167 (500 mL)
Autosampler Tubes – 50 mL, Conical, Free-Standing	B0193534

Titan MPS Digestion System	
Component	**Part Number**
Consumables Kit for Standard 75 mL Digestion Vessels	N3132000
Rupture Disks for Standard 75 mL Digestion Vessels (25 pieces)	N3132001
Pressure Seal for Standard 75 mL Digestion Vessels (10 pieces)	N3132002
End Cap Plug for Gas Containment Manifold	N3134004
Single Lip Seal Forming Tool for Standard 75 mL Digestion vessels	N3132015

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