



Monitoring Heavy Metals by Atomic Absorption Spectroscopy for Compliance with RoHS and WEEE Directives

Application Note

Semiconductor Analysis and Environmental

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Introduction

The rapid expansion in the quantity of used electronic and electrical appliances has created a need to safely dispose of the used equipment. The European Community has introduced regulations to enforce limits on the amount of toxic metals and organic chemicals used in the production of material. Compliance with the regulations will help prevent hazards for future generations when the equipment is recycled or responsibly disposed. In electronic and electrical equipment manufacturing, the regulations require these materials to be measured and limited.

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 AA, ICP-OES or ICP-MS [1-2]. Hexavalent chromium can be determined by UV-Vis [3-4], the PCB and PBDE can be determined by GC [5] and GC-MS [6-7]. On the other hand, XRF can also be used for screening heavy metals and total bromine [1,8]. In this article, various sample preparation methods are evaluated for the determination of Cd, Pb, Hg and Cr in plastic by atomic absorption spectroscopy.

In Varian ICP-OES Application Note Number 40, Tran Nahm [9] reported on the determination of metals in plastics using ICP-OES instrumentation. In this article, they report on the measurement of Cd, Cr, Pb and Hg in plastics using atomic absorption and Zeeman graphite furnace using the same analytical sample preparation processes.



Agilent Technologies

Instrumentation

All furnace measurements were performed using an Agilent 280Z AA spectrometer fitted with an Agilent PSD 120 Programmable Sample Dispenser.

The mercury vapor measurements were conducted using an Agilent 280FS AA operating in Duo mode with a VGA 76 Vapor Generation Accessory while the furnace analysis was underway on the Agilent 280Z AA.

Normal coded hollow cathode lamps were used for analysis of mercury, cadmium and chromium and an UltrAA lamp for lead.

A microwave digestion oven (CEM, Mars 5, ESP 1500 Plus, CEM Corporation, Mathews, NC) was used for the microwave digestions.

Table 1. Instrument Operation Conditions

Element	Cd	Pb	Cr
Instrument type	Zeeman	Zeeman	Zeeman
Concentration units	µg/L	µg/L	µg/L
Instrument mode	Absorbance	Absorbance	Absorbance
Sampling mode	Autonormal	Autonormal	Autonormal
Calibration mode	Concentration	Concentration	Concentration
Measurement mode	Peak area	Peak area	Peak area
Replicates standard	2	2	2
Replicates sample	2	2	2
Expansion factor	1	1	1
Minimum reading	Disabled	Disabled	Disabled
Smoothing	7 point	7 point	7 point
Concentration decimal places	1	1	1
Wavelength	228.8 nm	283.3 nm	357.9 nm
Slit width	0.5R nm	0.5 nm	0.2 nm
Gain	45%	36%	42%
Lamp current	4.0 mA	10.0 mA	7.0 mA
UltrAA Lamp	No	Yes	No
Lamp position	1	3	2
Background correction	On	On	On
Standard 1	1.0 µg/L	10.0 µg/L	5.0 µg/L
Standard 2	3.0 µg/L	25.0 µg/L	10.0 µg/L
Standard 3	5.0 µg/L	50.0 µg/L	20.0 µg/L
Reslope rate	0	0	0
Reslope lower limit	75.00%	75.00%	75.00%
Reslope upper limit	125.00%	125.00%	125.00%
Recalibration rate	0	0	0
Calibration algorithm	Quadratic origin	Quadratic origin	Quadratic origin
Calibration lower limit	20.00%	20.00%	20.00%
Calibration upper limit	150.00%	150.00%	150.00%
Total volume	27 µL	27 µL	22 µL

Element	Cd	Pb	Cr
Sample volume	20 µL	20 µL	20 µL
Volume reduction factor	2	2	2
Bulk concentration	5.0 µg/L	50.0 µg/L	20.0 µg/L
Bulk vial number	51	54	51
Makeup vial number	52	52	52
Sample number of injections	1	1	1
Sample last dry step	1	1	1
Hot inject	On	On	On
Hot inject temperature	80 °C	80 °C	80 °C
Hot inject rate	5	5	5
Modifier 1 mode	Co inject	Co inject	None
Modifier 1 volume	5 µL	5 µL	
Modifier	Ammonium dihydrogen orthophosphate (5 g/L)	Ammonium dihydrogen orthophosphate (5 g/L)	
Last dry step	0	0	
Injection rate	1	1	
Modifier 1 position	53	53	
Number of injections	1	1	

Table 2. Furnace Operating Conditions

Cadmium furnace conditions						
Step	Temperature (°C)	Time (s)	Flow (L/min)	Gas type	Read	Signal storage
1	85	30	0.3	Normal	No	No
2	110	10	0.3	Normal	No	No
3	400	5	0.3	Normal	No	No
4	400	5	0.3	Normal	No	No
5	400	2.5	0	Normal	No	Yes
6	1800	0.8	0	Normal	Yes	Yes
7	1800	2	0	Normal	Yes	Yes
8	1800	2	0.3	Normal	No	Yes

Lead furnace conditions						
Step	Temperature (°C)	Time (s)	Flow (L/min)	Gas type	Read	Signal storage
1	85	30	0.3	Normal	No	No
2	110	10	0.3	Normal	No	No
3	600	5	0.3	Normal	No	No
4	600	5	0.3	Normal	No	No
5	600	2.1	0	Normal	No	Yes
6	2100	0.9	0	Normal	Yes	Yes
7	2100	2	0	Normal	Yes	Yes
8	2100	2	0.3	Normal	No	Yes

Chromium furnace conditions						
Step	Temperature (°C)	Time (s)	Flow (L/min)	Gas type	Read	Signal storage
1	85	30	0.3	Normal	No	No
2	110	10	0.3	Normal	No	No
3	1000	5	0.3	Normal	No	No
4	1000	1	0.3	Normal	No	No
5	1000	2	0	Normal	No	Yes
6	2700	0.8	0	Normal	Yes	Yes
7	2700	2	0	Normal	Yes	Yes
8	2700	2	0.3	Normal	No	Yes

Table 3. Mercury Instrument Operating Conditions

Element matrix	Hg – RoHS
Instrument type	Vapor
Concentration units	µg/L
Sampling mode	AutoMix
Calibration mode	Concentration
Measurement mode	Integrate
Replicates standard	3
Replicates sample	3
Expansion factor	1
Minimum reading	Disabled
Smoothing	7 point
Concentration decimal places	2
Wavelength	253.7 nm
Slit width	0.5R nm
Gain	35%
Lamp current	4.0 mA
UltraA Lamp	No
Lamp position	4
Background correction	Off
Standard 1	20.00 µg/L
Standard 2	40.00 µg/L
Standard 3	60.00 µg/L
Reslope rate	0
Reslope lower limit	75%
Reslope upper limit	125%
Recalibration rate	0
Calibration algorithm	Quadratic origin
Calibration lower limit	20%
Measurement time	5.0 s
Pre-read delay	60 s
Vapor type	Cold vapor
Burner height	4.4 mm

Table 4. Characteristic Concentrations and Correlation Coefficients

	Lead	Chromium	Cadmium	Mercury
Characteristic concentration	1.8 µg/L	0.2 µg/L	0.10 µg/L	0.28 µg/L
Correlation coefficient	0.9999	1.0000	1.0000	1.0000

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:

- Institute for Reference materials and Measurements (IRMM)—European Reference Materials ERM-EC 681 Polyethylene 19 [10].
- National Metrology Institute of Japan (NMIJ) [11]—Certified Reference Material CRM 8102a ABS resin10.

Sample Preparation

Method BS EN 1122:2001 [12] is the only reference method for metal in plastics and provides details for the determination of Cd in plastic. There is no standard published sample preparation method for the determination of other heavy metals in plastic.

The use of sulfuric acid in Method EN1122 prevents the detection of Pb because of the potential precipitation of PbSO₄. On the other hand, EPA Method 3050 [13] Acid Digestion of Sediments, Sludges and Soils recommends the use of 1–2 g of sample in 10 mL HNO₃ and heating at 95 °C, and is not suitable for the analysis of plastics. Experiments show the 10 mL volume of HNO₃ is too small, and the heating temperature of 95 °C is not high enough to decompose the plastic material.

EPA Method 3053 [14] Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices, recommends microwave digestion with the use of HNO₃ and HF. Since HF is only required for samples of siliceous matrices, EPA Method 3051A [15] Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and oils (a microwave digestion method that uses only HNO₃) 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 5.

Table 5. Digestion Methods

Digestion methods	Analyte(s)
EN 1122 (H ₂ SO ₄ -H ₂ O ₂)	Cd
HNO ₃ -H ₂ O ₂	Cd, Pb, Cr
EPA 3051A (Microwave digestion with HNO ₃)	Cd, Pb, Cr, Hg

Method EN 1122 (H₂SO₄-H₂O₂ Digestion)

Accurately weigh 1 g of sample into a 250-mL beaker, add 10 mL of H₂SO₄, 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 H₂O₂ solution. Allow the reaction to subside after each addition. Heat again for about 10 minutes and allow to cool for 5 minutes. Add a further 5 mL portion of H₂O₂ solution and heat again. Stop the addition of H₂O₂ 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.

HNO₃-H₂O₂ Digestion

Accurately weigh 1 g of sample into a 250-mL beaker, add 25 mL of HNO₃, 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 H₂O₂. 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 to remove any organic plastic precipitate.

EPA Method 3051A (Microwave digestion with HNO₃)

Accurately weigh 0.5 g of sample into a fluorocarbon microwave vessel equipped with a controlled pressure relief mechanism. Add 10 mL concentrated HNO₃ 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 to remove any organic plastic precipitate.

MARS 5 Microwave Conditions

- Vessel: HP500
- Mode: Ramp to Temperature

Table 6. MARS 5 Microwave Conditions

Step	Power (w)	Percent	Ramp	Pressure (PSI)	Temperature (°C)	Hold
1	300	100	10	350	170	10
2	300	100	0.1	350	170	5

Results and Discussion

Analytical Results

Table 7. Analytical Results

Method	Chromium (mg/kg)	Lead (mg/kg)	Cadmium (mg/kg)	Mercury (mg/kg)
EN 1122 (H₂SO₄-H₂O₂ digestion)				
EC681	17.7	–	21.3	–
NMIJ	28.1	–	10.6	–
HNO₃-H₂O₂ digestion				
EC681	17.4	13.6	21.8	4.59
NMIJ	27.7	110.0	10.9	–
EPA Method 3051A (Microwave digestion with HNO₃)				
EC681	17.7	13.7	21.9	4.63
NMIJ	27.8	110.5	10.7	–
Certified concentrations				
EC681	17.6 ± 0.7	13.7 ± 0.8	21.7 ± 0.7	4.50 ± 0.15
NMIJ	27.87 ± 0.35	109.9 ± 0.89	10.77 ± 0.2	–

Detection Limits

The instrument detection limit is expressed as the concentration equal to three times the standard deviation of the blank concentration.

Table 8. Detection Limits

Element	WEEE/RoHS maximum (µg/kg)	Instrument detection limit (µg/kg)
Cadmium	100	0.015
Chromium	1000	0.089
Lead	1000	0.33
Mercury	1000	0.030

Conclusions

It should be noted that in the current regulations, the maximum level allowed for these metals in plastics are too high for normal graphite furnace measurement. The digested samples would require significant dilution before measurement leading to possible significant errors. This indicates that if a simple pass/fail test is required, the measurement of the lead, chromium and cadmium could be performed using flame atomization. Vapor generation would still be required for the determination of mercury.

However, the levels of metals present in the available reference materials are too low for flame atomization to yield accurate and precise measurements. This requires the use of graphite furnace measurements discussed in this application note. The limitation is the skill required to conduct the sample digestion. The measurement of lead, chromium, cadmium and mercury in polymers is shown to be very simple as the levels present in the analytical solutions are well above the instrument detection.

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Printed in the USA
February 1, 2012
SI-01638



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