

# Application Note – Determination of Plastics for Cd, Cr, Pb, and Hg

## **Introduction:**

There is growing pressure on industry to reduce certain key metals in plastic housings and electronic/electrical components for both consumer and industrial products. In the European Union, the Waste from Electrical and Electronic Equipment (WEEE) and the Reduction of Hazardous Substances (RoHS) Directives has targeted CrVI, Cd, Hg, and Pb. The legislation, 94/62/EC, specifically requires that these metals be monitored due to the quantities of electronics that end up as scrap in landfill sites. A target date of July 2006 has been set whereby these metals must be below accepted levels when producing new electronic equipment.

Plastics such as, Polyethylene, are being monitored for the above metals. Using conventional hotplate techniques, these polymers are often difficult to decompose without the accompanying loss of analytes due to the high temperatures involved.

This application note describes the use of a high temperature graphite block (*DigiPREP HT*) for sample preparation. European Reference Materials EC680 and EC681 Certified Plastic were used as reference materials.

## **Sample Type:**

Polyethylene  
Sample weight: 0.5 g

## **Supplies and Reagents:**

- 1) A 250 ml borosilicate *DigiTUBE*
- 2) *DigiPREP HT 250*
- 3) Touch Screen Controller
- 4) Boiling Rods (package of 40)
- 5) Analytical Balance
- 6) Calibrated Class “A” Volumetric Flask (50 ml)
- 7) H<sub>2</sub>SO<sub>4</sub> (98%) 10 ml
- 8) HNO<sub>3</sub> (70%) 50 ml
- 9) H<sub>2</sub>O<sub>2</sub> (30%) 20 ml
- 10) WEEE RoHS Releasing Reagent
- 11) Single Element Certified ICP-AES Standard 1000 ppm Cd, Cr, Pb, and Hg

## **Sample Preparation Procedure:**

**The Sample:** Cut the sample into small pieces and weigh out 0.5 g. Place the sample in the 250 ml Digestion Tube. Add 10 ml H<sub>2</sub>SO<sub>4</sub> (98%). Place the tubes in the rack. The rack should then be placed on the *DigiPREP HT*. Each sample batch should include a blank in duplicate and a spike recovery in duplicate. Add 0.5 ml of WEEE-RoHS Releasing Reagent to all tubes. The Hg and Pb should be in form of stable sulfate salts.

**The Blank:** The blank consist of the acids added to the tube without any sample.

**The Method Validation:** The method is validated using spiked recoveries and Certified Reference Materials. One milliliter of a certified spectrochemical single element standard for each element is added to a sample (see above). The spiked sample is then processed through the digestion procedure. The recoveries must be between 80 and 125% for each trace element for the method to be validated.

**The Digestion Procedure:** The tubes should be identified on the rack. The rack should be placed on the HT and the temperature profile found in Table 1 is initially used.

DigiPREP

# Application Note - Determination of Plastics for Cd, Cr, Pb, and Hg

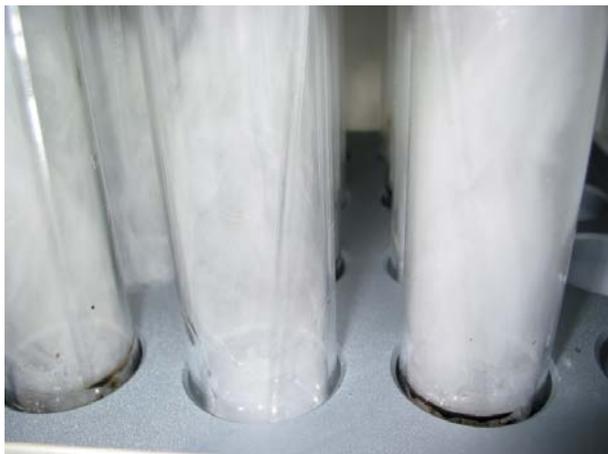


Image 3. The Sulphuric Acid Attacking the plastic at 380°C  
(Note: The digestion is complete when no more fumes are being produced.)

H<sub>2</sub>O<sub>2</sub> is then added in 5ml aliquots (The reaction will be quite vigorous). It should be added four times. The reaction should be allowed to diminish after each addition. When the reaction at room temperature has diminished, the sample is placed in the *DigiPREP HT* using the temperature profile found in Table 2.

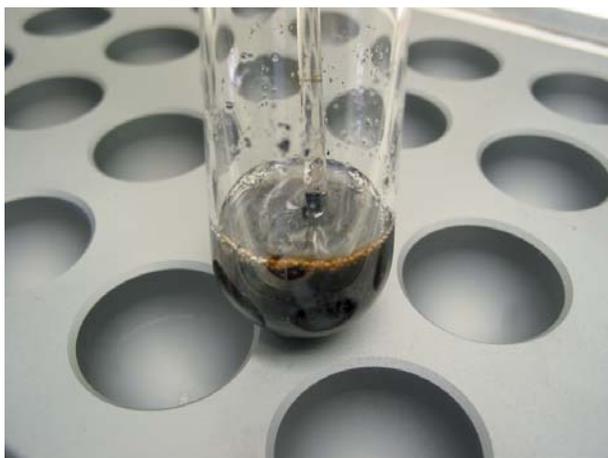


Image 4. The sample prior to H<sub>2</sub>O<sub>2</sub> addition

Table 2. Program 2-Temperature Profile for H<sub>2</sub>O<sub>2</sub>

Temperature (°C)	Time (min)	Ramp/Hold
160	20	Ramp
160	20	Hold
240	15	Ramp
240	25	Hold

The volume should be reduced to below 10 ml. The samples should then be cooled to room temperature. HNO<sub>3</sub> is then added in 1 ml aliquots. A maximum of 5 ml of HNO<sub>3</sub> should be added. The reaction should be allowed to diminish. The sample is then placed on the *DigiPREP HT* using the temperature profile found in Table 3.

DigiPREP

# Application Note - Determination of Plastics for Cd, Cr, Pb, and Hg

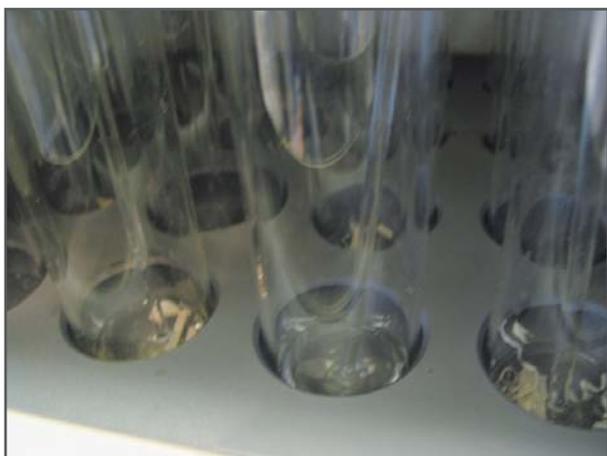


Image 1. The samples in the tube at the start of the digestion

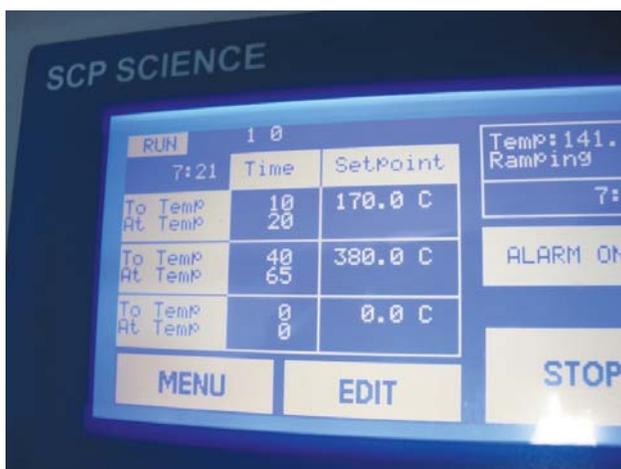


Image 2. Program 1 as seen on the touch screen controller

Table 1 Program 1- Temperature Profile for H<sub>2</sub>SO<sub>4</sub>

Temperature (°C)	Time (min)	Ramp/Hold
170	25	Ramp
170	10	Hold
340	40	Ramp
340	65	Hold

The sample will continue to digest until the white fumes are formed. The digestion should be continued until 1 ml or less remains in each tube. The samples are then cooled to room temperature. Add 1 ml of 5 ppm Al<sup>3+</sup> standard. The hg should be in form of a stable Hg<sub>2</sub>SO<sub>4</sub> salt.

Digiprep

# Application Note - Determination of Plastics for Cd, Cr, Pb, and Hg

Table 3. Program 3-Temperature Profile for HNO<sub>3</sub>

Temperature (°C)	Time (min)	Ramp/Hold
120	20	Ramp
120	30	Hold

The samples should be allowed to cool to room temperature and transferred to a 50 ml volumetric flask. The digestion tube should be washed three times with De-ionized water. The wash should also be transferred to the volumetric Flask.



Image 5. The samples after the transfer to 50 ml Volumetric Digestion vessel. The glass tubes are rinsed with water and it is used to complete to volume.

## Sample Analysis Procedure:

The samples were analyzed using Hitachi Graphite Furnace Atomic Absorption. The Hg was analyzed with the same instrument equipped with Hydride Generator. The method of known additions was used to correct for possible matrix effects. Each sample was divided into four aliquots. A multi-element standard was then added in small quantities (1 ml of a 100 ppm standard). This was done in order not to modify the sample matrix. The first aliquot received no additions, the second 1 ml, the third 2 ml and the fourth 3 ml. This technique is ideal for evaluating digestion methods without having to undertake the step of making matrix-matched samples. It is suggested to develop matrix matched calibration curve once the digestion method has been validated.

## Results:

Table 1 Results of Spike Recoveries

	Element (mg/kg)			
	Cd	Cr (Total)	Pb	Hg
% Recovery	97.37	98.45	99.69	93.23

Table 2 Results of EC 680

	Element (mg/kg)			
	Cd	Cr (Total)	Pb	Hg
Certified Value	140 +/- 2.5	114.6 +/- 2.6	107.6 +/- 2.8	25.3 +/- 1
HT Digestion	139.98 +/- 1.17	113.65 +/- 2.09	108.3 +/- 3.23	22.6 +/- 2.52

DIGIPREP

# Application Note - Determination of Plastics for Cd, Cr, Pb, and Hg

Table 3 Results of EC 681

	Element (mg/kg)			
	Cd	Cr (Total)	Pb	Hg
Certified Value	21.7 +/- 0.7	17.7 +/- 0.6	13.8 +/- 0.7	4.50 +/- 0.15
HT Digestion	21.03 +/- 1.52	17.73 +/- 1.62	14.20 +/- 0.98	4.23 +/- 0.78

## **Discussions:**

The sample digestion procedure worked well to reduce the violent bumping that occurs when the heated acid comes in contact with samples.

The addition of WEEE-RoHS releasing reagent improved the recoveries of Hg.

## **Conclusion:**

The method works well for the digestion of Polymers.

## **References:**

1. The certification of mass fractions of As, Br, Cd, Cr, Hg, Pb and S in two polyethylene CRMs.
2. The European Standard EN 1122:2001 Plastic Determination of Cadmium-Wet decomposition method.

Digiprep

**SCP SCIENCE**

Providing Innovative Solutions to Analytical Chemists

[www.scpscience.com](http://www.scpscience.com)

[sales@scpscience.com](mailto:sales@scpscience.com)

### **CANADA / USA**

Tel.: (800) 361-6820

Fax: (800) 253-5549

### **INTERNATIONAL**

Tel.: +1 (514) 457-0701

Fax: +1 (514) 457-4499

### **EUROPE**

Tel.: +33 (0) 1 69 18 71 17

Fax: +33 (0)1 60 92 05 67

### **CHINA**

Tel.: +86 (10) 58032301

Fax: +86 (10) 58032302