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APPLICATION NOTES

Consumer Product Safety Testing for Heavy Metal Content

Introduction

Lead is a toxic heavy metal that attacks the central nervous system causing blood and brain disorders, and has specifically been linked to learning disabilities in young children. Young children are especially at risk for lead poisoning, as they are more inclined to put things in their mouths. In 2004, the threat of lead poisoning from toy jewelry caused the Consumer Product Safety Commission (CPSC) to conduct a voluntary recall of over 150 million pieces of metal toy jewelry sold in vending machines. Other products containing lead have also been recalled including chalk, crayons, and children's products painted with lead-based paint. These recalls brought about the passage of the Consumer Product Safety Improvement Act (CPSIA) of 2008.

Section 102 of the CPSIA requires manufacturers to certify, via CPSC accredited third-party laboratories, that children's products comply with specific lead exposure limits. The original limit was set to 600 ppm lead by total weight and has since been lowered to 100 ppm for products and 90 ppm for lead in paint and coated surfaces for products intended for children ages 12 and under. CPSC staff developed Test Method CPSC-CH-E1001-08.2 and Test Method CPSC-CH-E1002-08.2 for measuring lead in metal and non-metal products using microwave digestion for sample preparation. Following microwave digestion, analysis can be performed using AA, GFAA, ICP or ICP-MS.

Using a MARS™ 6 system a wide variety of both metallic and non-metallic samples were digested. Standard reference materials were also incorporated in order to qualify results. All samples were analyzed on a Varian 720 ES ICP-OES spectrometer.

Instrumentation

A CEM MARS 6 with One Touch Technology© methods and PowerMAX™ power control was used to ensure complete and reproducible digestion conditions. The 55-mL MARSXpress™ vessel turntable was used, permitting up to 40 samples to be prepared simultaneously.

A Varian 720-ES ICP-OES instrument with axially viewed plasma and simultaneous CCD detection was used for all measurements. Sample introduction consisted of one piece standard quartz torch, glass double pass cyclonic spray chamber and SeaSpray nebulizer.

Experimental

Samples Analyzed

Many types of products, both metal and non-metal, were analyzed in order to prove the robustness of the method. In addition, reference standards were also digested and analyzed.

Non Metal Samples	
ERM-EC680k pellets	Multi colored fabric
ERM-EC681k pellets	Silver fabric
NMIJ CRM 8102-a pellets	Tassels –black, blue, yellow
NMIJ CRM 8103-a pellets	Hawaiian Lei
Lion Chips	Lion Ground
Bendable Toy Chips	Bendable Toy Ground
Mini Blind Chips	Mini Blind Ground

Metal Jewelry	
Leaf Pendant	Silver Pendant
Girl Pendant – Green	Gold Hoop Earring
Girl Pendant – Red	Silver Heart Earring
Girl Pendant – Multi Color	Whale Charm
Pink Elephant	

MARS 6

Sample Preparation

Non-Metal Products

Prior to digestion, the plastic samples were cut into small pieces. Not all of the samples were homogeneous. For comparison purposes, some of these samples were also freeze-dried and ground into a fine powder using a cryogenic mill. The CRMs were in the form of pellets.

Microwave-Assisted Digestion

Non-Metal Products

Reference Test Method CPSC-CH-E1002-08 was used as follows:

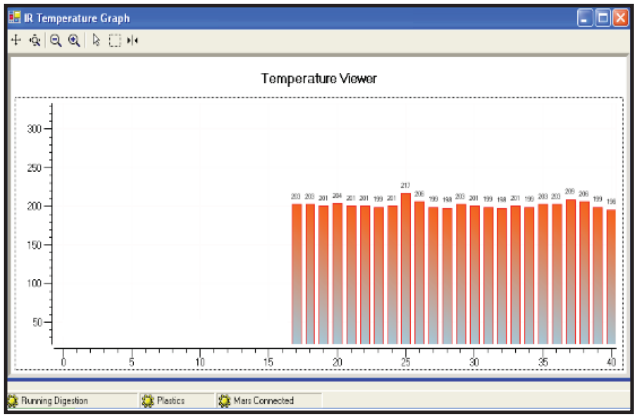
1) Weigh 200 mg of each sample (chipped, milled or pellets)
2) Place samples in microwave vessels (55-mL MARSXpress)
3) Add 5-mL concentrated HNO_3 to each vessel
4) Select method and digest, then allow the digested samples to cool to room temperature.
5) Transfer and dilute samples to 50 g with DI water

Table 1. Method Parameters for Non-Metal Products

MARS 6

Method	Ramp Time (mins)	Hold Time (mins)	Digestion Temperature (°C)
*CPST-Nonmetal	20	10	200

*CPST-Nonmetal is not a preprogrammed OneTouch method in the MARS 6. A custom method was programmed, as above, for this testing.



Metal Jewelry

Reference Test Method CPSC-CH-E1001-08 was used as follows.

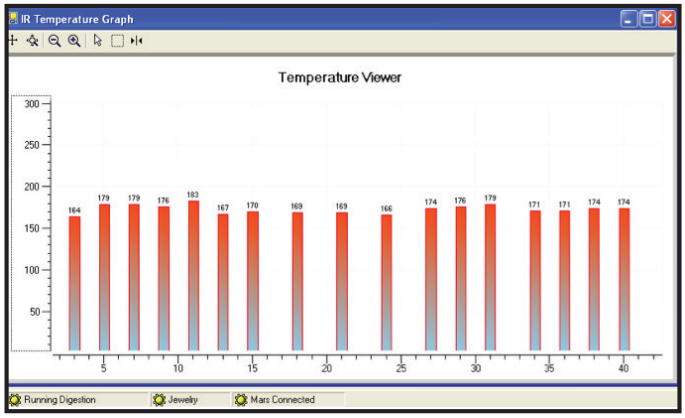
1) Weigh 100 mg of each sample (cut or ground)
2) Place samples in microwave vessels (55-mL MARSXpress)
3) Add 6 mL acid mixture (4.5-mL HNO_3 + 1.5-mL HCl) to each vessel
4) Select method
5) Transfer and dilute samples to 50 g with DI water

Table 2. Method Parameters for Metal Products

MARS 6

Method	Ramp Time (mins)	Hold Time (mins)	Digestion Temperature (°C)
*CPST-Metal	5:30	4:30	175

*CPST-Metal is not a preprogrammed OneTouch method in the MARS 6. A custom method was programmed, as above, for this testing.



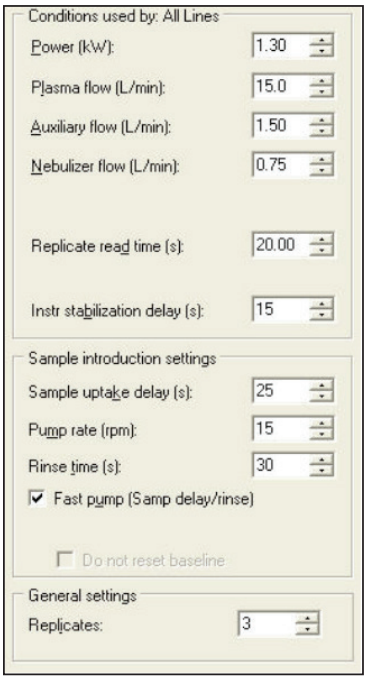
ICP-OES Analysis

A Varian 720-ES ICP-OES instrument with axially viewed plasma and simultaneous CCD detection was used for all measurements. The Varian 720-ES features an echelle polychromator equipped with a custom designed and patented CCD detector producing continuous wavelength coverage from 167 to 785 nm.

The sample introduction consisted of a one-piece standard quartz torch, glass double-pass cyclonic spray chamber and SeaSpray nebulizer. ICP Expert II software version 1.1.2 was used for instrument operations. An Yttruim internal standard was added on-line. Multi-element calibration standards were incorporated (Blank, 0.1, 1, 5 and 10 mg/kg).

All standards were matrix-matched for the reagents used in the sample preparation. Weight, volume, and dilution correction factors were automatically applied for samples and calibration solutions (wt/wt calculations). Fitted Background Correction was used, providing fast and accurate determination of background signals. Multiple wavelengths were monitored for most analytes to provide confirmation of results. A few solutions were diluted and rerun to confirm high results.

iCP-OES Instrument parameters as follows:



Results

Reference Materials

NMIJ CRMs – ABS Resin (Japan)

Units = mg/kg

Overall % RSD - 5 sample preparations over 2 days

CRM 8102-a	Pb	Cd	Cr
Measured Value	111.3	11.06	27.65
Certified Value	108.9 (0.89)	10.77 (0.20)	27.87 (0.35)
% Recovery	102.2	102.6	99.2
Overall % RSD	1.4	0.4	0.7

CRM 8103-a	Pb	Cd	Cr
Measured Value	1089	109	272.8
Certified Value	1084 (9.4)	106.9 (1.37)	269.5 (4.5)
% Recovery	100.5	101.9	101.2
Overall % RSD	1.2	0.9	0.5

Reference Materials

IRMM ERMs – Low Density Polyethylene (Europe)

Units = mg/kg

Overall % RSD - 5 sample preparations over 2 days

ERM-EC680k	Pb	Cd	Cr	As	Sb	Zn**
Measured Value	13.8	20.4	7 - 13.5	3.8	10.5	141
Certified Value	13.6 (0.5)	19.6 (1.4)	2.9 - 16.2	4.1 (0.5)	10.1 (1.6)	137 (20)
% Recovery	101.3	103.9	Not Certified	93.1	103.6	103
Overall % RSD	5.3	1.4		4.9	2.3	2.2

ERM-EC681k	Pb	Cd	Cr*	As	Sb	Zn**
Measured Value	99.4	141	43 - 70	26.9	96.9	1267
Certified Value	98 (6)	137 (4)	20 - 80	29.1 (1.8)	99 (6)	1250 (70)
% Recovery	101.4	102.9	Not Certified	92.4	97.9	101.4
Overall % RSD	2.2	0.9		2.3	3.1	2

* Acid Digestible Cr Only
** Not Certified - Indicative Value
Units = mg/kg
Overall % RSD - 5 sample preparations over 2 days

Results

Non-Metal Products
Units = mg/kg

	Pb	Cd	Cr	As	Sb	Zn
Lion Chips	225	13.5	5.4	1.8	169	172
Lion Ground	232	13.8	9.9	1.8	241	177
Bendable Toy Chips	3030	84.2	35.2	0.8	9.2	60.8
Bendable Toy Ground	3230	89.4	43.1	1.2	10.8	158
Mini Blind Chips	12000	135	57	1.3	1.1	9.9
Mini Blind Ground	13100	147	80.6	0.9	1.6	11.5
Multi Color Fabric	730	0.2	159	1.3	11	2320
Silver Fabric	164	350	5.8	1.8	9.2	160
Tassels - Black	153	0.1	0.5	0.6	1.2	69.2
Tassels - Blue	0.9	0.1	0.5	0.6	1.7	60.4
Tassels - Yellow	4360	0.1	965	1.3	13.2	91.3
Hawaiian Lei	1320	0.1	289	0.9	16.5	30.5

Highlight - CPSIA maximum Pb level exceeded

Results

Metal Jewelry
Units = mg/kg

	Pb	Cd	Cr	As	Sb	Zn
Leaf Pendant	48.3	88.6	4.4	3.4	10.5	81600
Girl Pendant - Green	877	1.9	149	18.9	14.6	1980
Girl Pendant - Red	500	1.6	80.5	10.9	12.8	1930
Girl Pendant - Multi Color	452	1.7	79.7	13.3	15.3	1940
Pink Elephant	55	0.3	13.4	16.1	4.3	192
Silver Pendant	34.3	0.5	4	2.7	6.2	81000
Gold Hoop Earring	270	7.5	1.4	7.2	20.6	72500
Silver Heart Earring	47500	23200	8.1	12.5	12.8	140000
Whale Charm	1050	3.9	1.6	14.4	31	62000

Highlight - CPSIA maximum Pb level exceeded

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APPLICATION NOTES

Summary:

The non-metal samples were processed together in a single MARS 6 batch (cut pieces, ground powders, and pellets). Considering the differences between sample types, the temperature spread was quite small during the hold portion of the digestion at 200 °C. No venting was observed during the run .

Excellent results were obtained on certified materials on both the NMIJ ABS resins and the ERM low-density polyethylene samples, including the volatile element arsenic. RSD's ranged from 0.4 to 5.3. The toy and mini-blind samples that were ground versus cut also showed good correlation.

Digested samples of the metal jewelry produced solutions from clear and colorless upon dilution to clear and blue, while others were hazy and some had undigested pieces. This was to be expected as the MARS 6 sample prep method was built followiing the CPST Act specifications. The Act specifies digestion for heavy metal extaction, not complete digest non-heavy metal components.

The source of samples was a combination of pre-2008 and post-2008 customer submitted samples. This group of samples was selected to show both the efficacy of the digestion versus a "spiked" sample and the actual need for such regulation and mandatory testing. The actual pre-regulatory levels of Pb and Cd effectively demonstrate the previous health hazard to which consumers were exposed.

Conclusions

Various samples of toys, jewelry, and materials used in toys and children's products were prepared for elemental analysis using microwave digestion. They were analyzed for heavy metals, including lead, using an axial view ICP-OES instrument. Following CPSC protocols, microwave digestion provided a robust and reproducible means to prepare the wide range of materials that require testing under CPSC guidelines. Up to twenty-four samples were simultaneously digested in twenty minutes or less in the MARS 6 and ICP-OES providing the throughput and accuracy needed by accredited testing laboratories.

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