

Heavy Metal Analysis for the Toy Industry by Inductively Coupled Plasma Optical Emission Spectroscopy

In support of the toy industry, many laboratories are being called upon to analyze a wide variety of sample matrices for metal content. The primary element of interest is lead, but a number of other toxic elements pose a considerable threat, especially for children. This subset of elements, known as heavy metals, includes antimony, arsenic, barium, cadmium, chromium, selenium, mercury and lead as they are all known to accumulate in the body and cause detrimental effects over time. Some plastic and wooden toys, particularly those with painted surfaces have demonstrated elevated levels of Pb and other elements. Regulations exist which provide limits in materials for which surface contact with children can result in possible ingestion. Analysis of toys and other items of interest for heavy metal content is necessary to validate their manufacture, distribution and sale.

Different regulating agencies provide elemental content limits for a variety of these sample types. The European Standard for safety of toys, EN 71, Part 3, which is adopted into ISO 8124-3, contains one section entitled “Migration of certain elements”. In this section it defines the limits of element migration from toy materials (see Table 1). In the U.S., the Food and Drug Administration (FDA) regulates the amount of lead and cadmium that can be leached from ceramic and other hollowware and flatware. As these items are designed to contain food, potential exposure to cadmium and lead must be limited. They specify an acetic acid leach procedure, similar to the hydrochloric acid leach specified in ISO 8124-3. Tables 2 and 3 list the limits detailed in these regulations. Further U.S. safety standards for toys are described by the Consumer Product Safety Council (CPSC) and listed in ASTM 936-07 including a reference to EN 71, Part 3. Lead in paint applied to toys is regulated in the Code of Federal Regulations (16 CFR 1303) which bans paint containing more than 0.06% lead in the dried paint film. The CPSC also bans any toys or articles intended for use by children that bear this lead-containing paint. These articles can also include any products that are used in or around the household or in recreation that may pose a risk to children of lead poisoning such as mini-blinds.

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Table 1. Limits of Element Migration from Toy Materials (ISO 8124-3).

Element	Sb	As	Ba	Cd	Cr	Pb	Hg	Se	
Maximum migrated element in mg/kg toy material	Any toy material given in clause 1 except for:								
modelling clay	60	25	1000	75	60	90	60	500	
Modelling clay	60	25	250	50	25	90	25	500	

Table 2. Ceramic Leachable Lead Limits.

Category	Criteria	Guidelines micrograms/mL
Flatware	average of 6 units	3.0
Small Hollowware other than cups and mugs	any one of 6 units	2.0
Cups/mugs	any one of 6 units	0.5
Large Hollowware other than pitchers	any one of 6 units	1.0
Pitchers	any one of 6 units	0.5

Table 3. Ceramic Leachable Cadmium Limits.

Category	Criteria	Guidelines micrograms/mL
Flatware	average of 6 units	0.5
Small Hollowware	any one of 6 units	0.5
Large Hollowware	any one of 6 units	0.25

Although the actual analysis of these elements is not generally complicated, appropriate sample preparation can be challenging. It is important to evaluate the individual regulation requirement as it pertains to sample leaching or decomposition. To simulate the actions of the human digestion system, some sample preparation techniques utilize specific leaching procedures. Others require a complete and total acid decomposition of the sample to ensure a full content analysis. If the entire product is used in the extraction, contributions from the substrate or interior material in addition to the paint may be evaluated. Regulations may require paint scraping for evaluation of paint content only. It is important to understand the differences between whole-product versus paint-only sampling as well as between leaching and complete dissolution techniques.

Following sample preparation, the measurement of elemental content can be carried out in any number of ways such as atomic absorption (AA), inductively coupled plasma-optical emission spectroscopy (ICP-OES) or inductively coupled plasma-mass spectrometry (ICP-MS).

For this work, the ICP-OES technique was chosen as it provides both sufficient detection limits for the elements of interest and multielement capability with reasonable cost and experience requirements. The measurements were performed using the PerkinElmer® Optima™ 5300 DV instrument. However, the details specified in this method can also be applied to the Optima 2100 DV instrument as well.

Sample preparation

A variety of matrices (Figures 1-3) were analyzed to show performance at the concentration levels of interest. Three different sample preparation methods were used to satisfy the various regulating agencies:

- Extraction – U.S. method AOAC 973.32
– 4% acetic acid, 24 hours in darkness
- Extraction – European method EN 71, Part 3 (ISO 8124-3)
– HCl for 2 hours at 37 °C, darkness
- Complete paint digestion
– Microwave, Multiwave™ 3000, diluted to 50 mL



Figure 1. Toy car samples.



Figure 2. Additional toy samples.

For the two extraction methods, the paint was scraped off the toys and approximately 100 mg was weighed into a plastic 50 mL volumetric tube. To each tube, 10 mL of 4% acetic acid or 5 mL of 0.1 M HCl was added. For the acetic acid extractions, the tubes were allowed to sit overnight in darkness (up to 24 hours). The tubes containing the HCl extractant were heated in a water bath at 37 °C in darkness for 1 hour with agitation. This was followed by 1 hour in the water bath in darkness without agitation. These extractions were then filtered through 0.45 µm membranes prior to analysis.



Figure 3. Toy train samples.

The complete digestion was carried out using the Multiwave 3000 microwave digestion system equipped with the Rotor 8XF100. The Multiwave 3000 offers closed vessel technology which allows for complete digestion of difficult substances as well as consistent results. Approximately 100 mg of sample was weighed into the sample vessels to which was added 6 mL HNO₃ and 1 mL HCl. The digestion program used is listed in Table 4. After digestion, the samples were quantitatively transferred to sample vials and diluted to 50 mL with deionized water.

Experimental

Analysis of all sample digests and extractions was performed using an Optima 5300 DV ICP-OES equipped with a SeaSpray concentric nebulizer (Glass Expansion, Pocasset, MA) and cyclonic spray chamber. The instrumental parameters are presented in Table 5. The wavelengths chosen are shown as part of the element name in Table 6.



Figure 4. The Multiwave 3000.

Table 4. MW3000 Digestion Program.

Step	Power (W)	Ramp (minutes)	Hold (minutes)	Fan
1	800	5	10	1
2	1100	10	15	1
3	–		15	3

Results and discussion

The U.S. extraction method using acetic acid and the European hydrochloric acid extraction were compared to see if the results were significantly different in the amount of lead and cadmium extracted and available for determination. Detection limits in solution (three times the standard deviation of the blank) are similar for the matrices and are listed in Table 6 for the acetic acid matrix. The results for a variety of toys are presented in Table 7. The amount in solution was back calculated to the solid material to provide a more accurate comparison. The results are similar in that the large amount of lead clearly exceeding the criteria for lead paint was identified (>600 mg/kg) by both methods. The HCl extraction does seem more aggressive as evidenced by generally larger lead values extracted from the samples.

Table 5. ICP-OES Instrumental Conditions.

Parameter	Setting
RF Power	1450 W
Nebulizer Flow	0.55 L/min
Auxiliary Flow	0.2 L/min
Plasma Flow	15.0 L/min
Sample Pump Flow	1.2 mL/min
Plasma Viewing	Axial
Processing Mode	Area
Auto Integration	5 sec min-20 sec max
Read Delay	30 sec
Rinse	30 sec
Replicates	3
Background Correction	one or two points
Spray Chamber	Cyclonic
Nebulizer	SeaSpray

Table 6. Calculated Detection Limits in Acetic Acid Matrix.

Analyte	Detection Limit (mg/L)
Sb 217.582	0.001
As 188.979	0.007
Ba 233.527	0.003
Cd 228.802	0.0004
Cr 267.716	0.001
Pb 220.353	0.003
Hg 194.168	0.001
Se 196.026	0.011

The European hydrochloric acid extraction method is referenced as the method of choice for toys in ASTM standard 936-07. It was further explored for a variety of toys using the variability factors and comparing the limits listed in the method. Table 8 shows the results for the eight elements listed in the method. The shaded boxes show values that exceed the values specified in the standard (listed in the table footnote). The yellow car exceeds the limits for barium, chromium, and lead.

Extractions present reproducibility problems (as seen in the variability factors for the HCl method) and do not often have reference materials certified for use in that manner. A complete digestion and analysis provides a more conservative result and can often be verified with a certified reference material. Two NIST paint reference materials were digested in duplicate using the Multiwave 3000 microwave digestion system with the same method as used for the toys and the eight elements of interest were measured. Table 9 shows the reference materials duplicate analyses and the recovery of the certified value.

Paint scraped from a variety of toys was also digested using the microwave procedure and the eight elements measured. The results are shown in Table 10. Several elements are present and lead is clearly above the leaded paint limits in the yellow plastic car.

Table 7. Comparison of Acetic Acid and HCl Leaching Procedures (mg/kg).

	Hydrochloric Acid Extraction		Acetic Acid Extraction	
	Lead	Cadmium	Lead	Cadmium
Orange Wooden Spoon	< DL	< DL	< DL	< DL
Purple Wooden Spoon	< DL	0.1	< DL	0.1
Red Wooden Spoon	< DL	< DL	< DL	< DL
Pink Charm	< DL	< DL	< DL	< DL
Blue Charm	0.1	< DL	< DL	< DL
Purple Charm	0.1	< DL	< DL	< DL
Red Wooden Car Puzzle Piece	0.3	< DL	0.4	< DL
Yellow Wooden Car Puzzle Piece	0.4	< DL	< DL	< DL
Yellow Plastic Car	2490	< DL	1115	< DL

Conclusion

Hazardous element content in toys is an on-going concern. This paper has shown that ICP-OES can accurately measure a wide range of concentrations and elements. The suite of eight elements specified in the European method

can be increased to cover additional elements in the same run if additional elements are regulated or for liability concerns. ICP-OES coupled with a digestion technique, such as microwave, can provide a fast turn-around so that waiting shipments can be evaluated as soon as possible for release.

Table 8. HCl Extract Results for Eight Elements (mg/kg).

	Antimony	Arsenic	Barium	Cadmium	Chromium	Lead	Mercury	Selenium
Orange Wooden Spoon	< DL	< DL	51.2	< DL	< DL	< DL	< DL	< DL
Purple Wooden Spoon	< DL	< DL	69.5	0.1	0.1	< DL	< DL	< DL
Red Wooden Spoon	< DL	< DL	71	< DL	< DL	< DL	< DL	0.002
Pink Charm	< DL	< DL	5.1	< DL	0.1	< DL	< DL	< DL
Blue Charm	< DL	< DL	4.8	< DL	< DL	0.1	< DL	< DL
Purple Charm	< DL	< DL	4.9	< DL	< DL	< DL	< DL	< DL
Red Wooden Car Puzzle Piece	< DL	0.6	568	< DL	1.1	0.2	< DL	< DL
Yellow Wooden Car Puzzle Piece	< DL	0.3	666	< DL	1.0	0.3	< DL	< DL
Yellow Plastic Car	2.1	0.4	1020	< DL	383	1740	0.3	< DL

Calculations based on total amount extracted and factor for variability as described in the method.
Limits: Sb 60, As 25, Ba 1000, Cd 75, Cr 60, Pb 90, Hg 60, Se 500.
< DL: less than the calculated detection limit.

Table 9. NIST Standard Analysis.

	Pb in Solution (mg/L)	Standard Deviation (SD)	Pb in solid	% Recovery
NIST 1579a High Lead Paint-1	122.1	3.2	11.74%	97.8
NIST 1579a High Lead Paint-2	138.2	3.6	11.85%	98.8
NIST 2582 Low Lead Paint-1	0.287	0.002	214 mg/kg	103
NIST 2582 Low Lead Paint-2	0.222	0.006	197 mg/kg	94.2

Table 10. Total Digestion Results for Paint (mg/kg).

	Antimony	Arsenic	Barium	Cadmium	Chromium	Lead	Mercury	Selenium
Red Train Engine 1	< DL	< DL	< DL	< DL	< DL	573	< DL	< DL
Red Train Engine 2	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL
Caboose	< DL	< DL	88	< DL	< DL	< DL	< DL	< DL
Yellow Crossing Sign	< DL	< DL	66	< DL	< DL	< DL	< DL	< DL
Red Wooden Car Puzzle Piece	< DL	8	2350	< DL	5	< DL	5	< DL
Yellow Wooden Car Puzzle Piece	< DL	< DL	3170	< DL	7	< DL	< DL	< DL
Yellow Plastic Car	600	14	104	< DL	3400	14800	6.0	< DL
NIST 1579a High Lead Paint	< DL	45	2.7%	20	200	11.8%	< DL	< DL
NIST 2582 Low Lead Paint	< DL	11	1860	< DL	30	205	6.0	< DL

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