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## Lead and Other Toxic Metals in Toys Using XRF Screening and ICP-OES Quantitative Analysis

### Introduction

From 2007 to 2008, the number of recalls for toys exceeding the U.S. limits set for lead dropped 43%. This represents however, more than 300,000 individual products posing potential hazardous exposure for children. The Consumer Product Safety Improvement Act of 2008 (CPSIA 2008) defines a children's product as a product primarily used by a child under the age of 12 and defines new levels of lead allowed in those products<sup>1</sup>. Allowable lead in painted surfaces will be reduced from 600 mg/kg to 90 mg/kg one year from enactment of the legislation (enactment date:

August 14, 2008). Allowable total lead content (surface and substrate) is reduced from 600 mg/kg to 100 mg/kg, incrementally over the course of three years. The American Academy of Pediatrics suggests that a level close to the background level in soil of 40 mg/kg would be most protective of children's health<sup>2</sup>.

Currently, EN-71, Part 3 and ASTM 963 specify evaluation of the toy by soaking in a mild hydrochloric acid solution at body temperature and measuring the accessible metal extracted into the solution. If a coating can be separated, a total analysis of the coating to comply with lead content requirements can be done. CPSIA 2008 provides no exemption for electroplated substrates, so that a total analysis on both coating and substrate must be done, though little other measurement guidance is currently available. EN-71 may also be revised in the near future to add other hazardous elements, such as aluminum, cobalt, copper, nickel, and others. The evolving need to measure lead and other metals at increasingly lower levels makes information on analysis technologies and performance valuable in making knowledgeable decisions.

A variety of techniques can be used to meet the regulations, including atomic absorption (both flame FLAA and graphite furnace GFAA), inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). Hand-held energy dispersive XRF, requiring minimal or no sample preparation can provide a way to screen products on-site as to determine whether further quantitative analysis is required.

The techniques are compared for several parameters in Table 1.

Since the techniques in Table 1 have different characteristics, which would be the most suitable for the variety

of children’s products, including toys that may require analysis? This question is addressed in this work using ICP-OES and hand-held XRF to examine a variety of toy materials. Ease of use and agreement between techniques at the current level for lead were evaluated.

### Experimental

A variety of children’s toys were obtained randomly from a church nursery room and other sources. One known recalled item, Boy Scout totem badges of differing ages were also obtained. Figure 1 shows the variety of toys, including fabric, soft and hard toys and some with painted surfaces.

**Table 1. Comparison of Several Analysis Techniques for Lead Determination (mg/kg).**

	GFAA	ICP-OES	ICP-MS	Hand-held XRF
Estimated detection limit for lead*	0.025	0.5	0.025	NA**
Sample prep required	Yes	Yes	Yes	No
Simultaneous multielement	No	Yes	Yes	Yes

\* Includes a 500x dilution to account for sample preparation for GFAA, ICP-OES, and ICP-MS. Detection limits can be further improved if a smaller dilution is used.  
 \*\*NA: screening tool, detection limits matrix driven.



Figure 1. Variety of toys measured.

**Table 2. Microwave Digestion Program.**

Power (W)	Ramp (min)	Hold (min)	Fan
500	5:00	15:00	1
900	10:00	15:00	1
0		20:00	2

**Table 3. ICP-OES Instrumental Conditions.**

Instrument	Optima 7300 DV ICP-OES
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 (Glass Expansion®, Pocasset, MA)

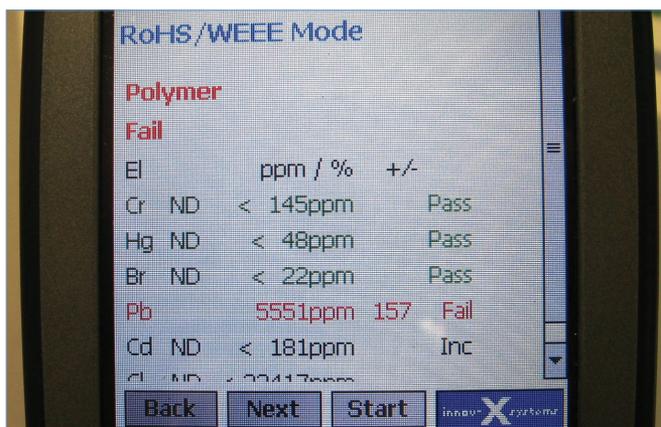


Figure 2. XRF result screen.

Samples were prepared for ICP-OES analysis by scraping off the paint or cutting the substrate into small pieces. Approximately 0.01-0.1 g was weighed into a PTFE microwave digestion vessel and 6 mL of concentrated nitric acid (GFS Chemical®, Columbus, Ohio) and 1 mL of concentrated hydrochloric acid (GFS Chemical®, Columbus, Ohio) were added. The samples were placed in the Multiwave™ 3000 microwave digestion system (PerkinElmer, Shelton, Connecticut) and digested according to the program shown in Table 2.

The Optima™ 7300 DV was used for analysis of the full suite of elements currently regulated in EN-71, Part 3<sup>3</sup> and referenced in ASTM D963<sup>4</sup>, and CPSIA, including lead. The conditions are as shown in Table 3.

The Innov-X® Import Guard model was used for all hand-held XRF measurements, and a general calibration was performed. For analysis of the same samples with XRF, no sample preparation was required. The system uses energy dispersive X-ray fluorescence and easily identifies

elements over a wide dynamic concentration range, from ppm levels up to virtually 100% by weight. An example of the result obtained on the screen is shown in Figure 2.

## Results and Discussion

The analysis of the toys by hand-held XRF and ICP-OES are shown in Table 4. The check mark in the XRF column indicates the XRF analysis displayed a lead value higher than the limit of 600 mg/kg in the screened toy indicating further quantitative analysis is recommended. The value determined by ICP-OES confirms that the value was higher than the regulatory limit in the coating or for a total analysis of the substrate material. In this case, the value measured with XRF is not reported although the value would give further refinement of the concentration for the elements measured.

Detection limits for the ICP-OES are shown in Table 5 for both the digested solution and the amount in the original material. Since the amount taken for digestion may vary and the dilution can be changed, a 500x dilution was assumed for the calculation. This represents a typical 0.1 g of material diluted to a final volume of 50 mL.

Duplicate sample preparation and analysis of several samples can indicate the reproducibility of the method, provided the samples are homogeneous. Table 6 shows the results for duplicate sample preparation and analysis of three different types of samples. The fabric and the uniformly-colored plastic show good agreement between the duplicate analyses (less than 20% relative percent difference). The puzzle board required scraping paint from the surface for analysis and it was difficult to uniformly remove only the paint without taking some of the substrate, as shown in Figure 3. This may contribute to the very different values obtained for the duplicate analysis.



Figure 3. Puzzle board and scrapings.

Table 4. Results for Toys Measured with XRF and ICP-OES (mg/kg).

	XRF	Antimony	Arsenic	Barium	Cadmium	Chromium	Lead	Mercury	Selenium
Toy Stove Knob	√	32	<DL	2	4	773	3950	<DL	13
Yellow Mega Block	√	12	<DL	56	3	774	3690	<DL	27
Badge-1 New (Yellow Paint)	√	<DL	<DL	16900	14	7340	34500	<DL	85
Badge-2 Older (Yellow Paint)	√	<DL	<DL	21200	2	8870	42100	<DL	20
Yellow Baby Rattle	√	<DL	<DL	70	<DL	544	2970	<DL	8
Yellow Crib Toy Holder Strap	√	15	<DL	146	<DL	377	1900	<DL	<DL
Green Cup		<DL	<DL	3220	2260	4	17	<DL	6
Red Ring		<DL	<DL	91	4	3	15	<DL	8

**Table 5. Estimated Detection Limits.**

Element	Detection Limit in Solution (mg/L)	Detection Limit in Solid (mg/kg)
Antimony (271 nm)	0.008	3.8
Arsenic (189 nm)	0.002	1.2
Barium (233 nm)	0.004	1.9
Cadmium (228 nm)	0.002	1.1
Chromium (267 nm)	0.003	1.6
Lead (220 nm)	0.010	6.4
Mercury (254 nm)	0.005	2.2
Selenium (196 nm)	0.011	5.7



Figure 4. Yellow ball measured in replicate.

**Table 6. Duplicate Sample Preparation and Analysis (mg/kg).**

	Antimony	Arsenic	Barium	Cadmium	Chromium	Lead	Mercury	Selenium
Green Fabric	15	<DL	302	<DL	332	1780	<DL	<DL
Green Fabric - Duplicate	13	<DL	329	<DL	362	1940	<DL	<DL
Puzzle Board	919	<DL	14	4	21,200	121,000	<DL	49
Puzzle Board - Duplicate	2187	<DL	5	5	14,600	82,600	<DL	15
Yellow Handle	<DL	<DL	360	<DL	1310	4990	<DL	<DL
Yellow Handle - Duplicate	<DL	<DL	336	<DL	1200	4620	<DL	12

A more extensive analysis of reproducibility is shown in Table 7. The standard deviation of five separate digestions and analyses for a yellow ball (Figure 4) show excellent precision.

It is interesting to note the lead level is high, in agreement with the XRF analysis. Several other elements, such as chromium, are also high. The XRF value reported for lead in the ball was 3940 mg/kg.

Regulations are continually changing and may require different elements to be monitored in the future, at different concentration levels. One way to help in preparing for that eventuality is the use of the universal data acquisition (UDA) feature, exclusive to the Optima ICP-OES software. In this case the Optima ICP-OES collects data for all of the wavelengths all of the time. If a standard is run at the time of the original data acquisition that includes more elements than the elements of interest at that moment, other elements can be measured with good quantitative accuracy by reprocessing at a later date. If an elemental concentration is of interest for an element that was not included in any of the usual multi-element standards, reprocessing can provide a semiquantitative result, usually within  $\pm 30\%$  of the true value.

Table 8 shows an example for a hydrochloric acid extract from a toy, extracted and measured using procedures specified in EN-71, Part 3. Both the original set of elements reported and the elements determined later (in blue) by reprocessing the data to examine the information previously stored for those elements are listed. This can be useful in assessing samples that may have been disposed or in better understanding the scope of samples in preparing for future analyses.

**Table 7. Analysis of Five Replicate Samples of a Yellow Ball.**

Element	Average (mg/kg)	SD
Antimony (271 nm)	10.6	0.49
Arsenic (189 nm)	12.4	1.8
Barium (233 nm)	707	3.1
Cadmium (228 nm)	78.3	0.73
Chromium (267 nm)	414	2.3
Lead (220 nm)	1980	9.7
Selenium (196 nm)	16.3	1.3
Mercury (254 nm)	<DL	-

## Conclusion

The regulatory landscape of toy measurements for hazardous metals is changing and will continue to change as elements, concentrations, and sample preparation procedures are refined and harmonized between the U.S. and Europe. Indeed, the lowest limits of 90 and 100 ppm are designated as what the CPSC deems to be feasible at the time and lower limits may be regulated in the future.

ICP-OES is the accepted certifying tool in determining a wide variety of metals that may contaminate toys, either in the substrate or a paint coating. Lead can be determined at the current 600 mg/kg concentration level permitted and the ICP-OES has sufficient detection capability that the new limits of 90 mg/kg can be reliably detected.

**Table 8. Universal Data Acquisition for Additional Elemental Data.**

Element	mg/kg extracted from solid
Antimony (271 nm)	6.7
Arsenic (189 nm)	1.5
Barium (233 nm)	1850
Cadmium (228 nm)	< DL
Chromium (267 nm)	655
Lead (220 nm)	2900
Selenium (196 nm)	< DL
Aluminum (396 nm)	438
Cobalt (228 nm)	< DL
Copper (327 nm)	< DL
Manganese (257 nm)	< DL
Nickel (231 nm)	< DL
Tin (189 nm)	< DL
Zinc (206 nm)	1230

ICP-OES and XRF are complementary techniques that work well together at the current regulatory level of 600 mg/kg. XRF provides rapid screening with a high degree of confidence when the sample is contaminated with lead. Highly accurate ICP analyses can be efficiently directed to the samples most likely contaminated using hand-held XRF's quick screening and no-sample prep characteristics. Samples identified as contaminated can be prepared and analyzed by ICP with less wasted time on uncontaminated samples, because of the positive screening result. As the limits are lowered, XRF will continue to perform as a screening technique, with ICP-OES providing confirmation with regulatory requirements.

## References

1. Consumer Product Safety Improvement Act, <http://www.cpsc.gov/ABOUT/Cpsia/legislation.html>
2. Testimony of Dana Best, MD, MPH, FAAP on behalf of the American Academy of Pediatrics, [http://www.aap.org/visit/coeh/COEH\\_Ltr\\_2007-09-20\\_Lead\\_Testimony.pdf](http://www.aap.org/visit/coeh/COEH_Ltr_2007-09-20_Lead_Testimony.pdf)
3. EN-71, Part 3 The Safety of Toys, Migration of Certain Elements, may be purchased from [http://www.standardsuk.com/shop/products\\_view.php?prod=26164](http://www.standardsuk.com/shop/products_view.php?prod=26164)
4. ASTM D-963-07, Standard Consumer Safety Specification for Toy Safety, may be purchased from <http://www.astm.org>