

# Application Note

## Use of Ultrasonic Nebulization with ICP-AES for Enhanced Detection of Regulated Elements in Toys

*Fred G. Smith, Teledyne CETAC Technologies, 14306 Industrial Road, Omaha, NE 68144-3334 USA fsmith@cetac.com*

### INTRODUCTION

Per the European Standard EN-71 Part 3, regulated elements in toy materials include 17 elements: Al, As, B, Ba, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Se, Sn, Sr, and Zn. These toy materials include coatings such as paint and a variety of component types: ceramic, glass, metal, polymer, wood, and textiles (natural or synthetic). Inductively coupled plasma atomic emission spectrometry (ICP-AES) is one technique that can be used for rapid measurement of these elements at mg/kg levels.

This application note will examine the use of an efficient ultrasonic nebulizer (USN) with axial-viewing ICP-AES for enhanced detection of the above listed elements in toys. Experimental parameters include ultrasonic nebulizer installation steps to the host ICP-AES instrument, sample preparation in dilute hydrochloric acid, reagent addition for improved measurement of boron (D-mannitol) and mercury (L-cysteine), and optimization of ICP-AES power and gas flows when using the USN. Figures of merit will include instrument detection and quantitation limits and measured concentrations of regulated elements from a variety of toy samples.



**Figure 1. Assorted toy samples include painted wooden blocks, plastic stacking rings, and a fake moustache. All samples are EN-71 Part 3 Category III sample types.**



**Figure 2a. Teledyne CETAC U5000AT+ Ultrasonic Nebulizer**

### EQUIPMENT & REAGENTS

Following are lists of primary equipment and reagents used for toy sample preparation and sample analysis.

#### Equipment:

1. ICP-AES: Optima 5300DV, PerkinElmer, Shelton, CT USA
2. Ultrasonic Nebulizer: U5000AT<sup>+</sup>, Teledyne CETAC Technologies, Omaha, NE USA
3. Block digestion system: DigiPREP Jr., SCP Science, Baie D'Urfe, Quebec, Canada
4. 10-mL polycarbonate Luer-Lok™ syringes, Becton Dickinson, Franklin Lakes, NJ USA
5. 0.45 mm PTFE filters, 13mm diam., Whatman®, Piscataway, NJ, USA

#### Reagents:

1. Hydrochloric acid, Optima grade, Fisher Scientific, Fairlawn, NJ, USA
2. Hydrogen Peroxide, TraceSelectGrade, >30%, Fluka Analytical, Sigma Aldrich Chemie, Steinheim, Germany
3. Various single element standards, Inorganic Ventures, Christiansburg, VA, USA
4. D- Mannitol, TraceSelect® grade, > 99.9999%, Fluka Analytical, Sigma Aldrich Chemie, Steinheim, Germany.
5. L-Cysteine, > 97%, SAFC, St. Louis, MO, USA



Figure 2b. Teledyne CETAC U5000AT<sup>+</sup> USN in operation

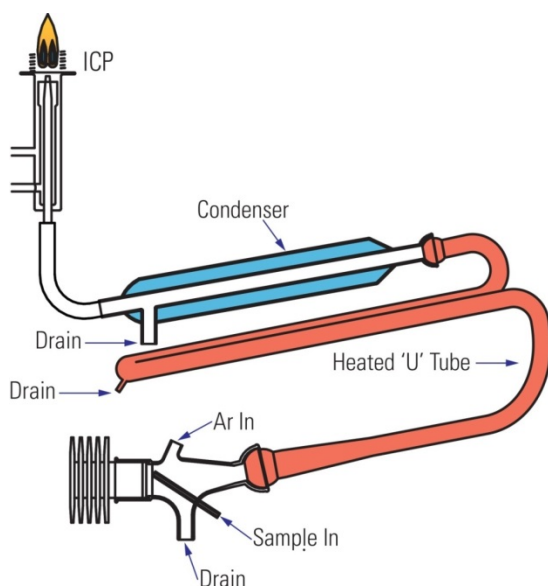


Figure 3. Ultrasonic Nebulizer Schematic

### SAMPLE PREPARATION

**Plastic Stacking Ring:** Three samples were cut with a fresh razor blade: 0.542g, 0.672g, and 0.713g; two samples were added to individual, precleaned 50-mL polypropylene (PP) tubes and one sample to a borosilicate glass vial.

**Fake Moustache Fiber:** Three samples were trimmed with a scissors: 0.380g, 0.410 g, and 0.400g; two samples were added to individual, precleaned 50-mL (PP) tubes and one sample to a borosilicate glass vial.

**Red Paint from Wooden Blocks:** The red paint was carefully removed from a series of wooden blocks using a

sharp razor: 0.103g, 0.102g, and 0.101g; two samples were added to individual, precleaned 50-mL (PP) tubes and one sample to a borosilicate glass vial.

**Hydrochloric Acid Solutions:** Three stock solutions of 0.07M HCl (high-purity grade) were prepared: one 0.07M HCl/0.4% $H_2O_2$  solution, one 0.07M HCl solution with 0.01% (w/v) L-Cysteine, and one 0.07M HCl solution with 0.2% (w/v) D- Mannitol. The added L-Cysteine improves Hg washout and the D-Mannitol improves B washout; 0.07M / 0.4%  $H_2O_2$  alleviates As species transport effects in the USN.

**0.07M HCl Reagent Addition:** Of the three sample types, one replicate sample was for Hg, one replicate sample for B, and the third sample for the other 15 elements. A solution mass of  $\sim 100x$  the sample weight was added to each red paint sample; a solution mass of  $\sim 50x$  the sample weight was added to each stacking ring and moustache fiber sample.

Sample tubes were placed in the block digestion system at 37°C for one hour in darkness with manual agitation every two minutes followed by another hour at 37°C in darkness with no agitation.

Samples were then carefully filtered through 0.45 mm PTFE filters to remove paint flakes and fibers.

### STANDARDS PREPARATION

Following are details of multielement, boron, and mercury standards preparation.

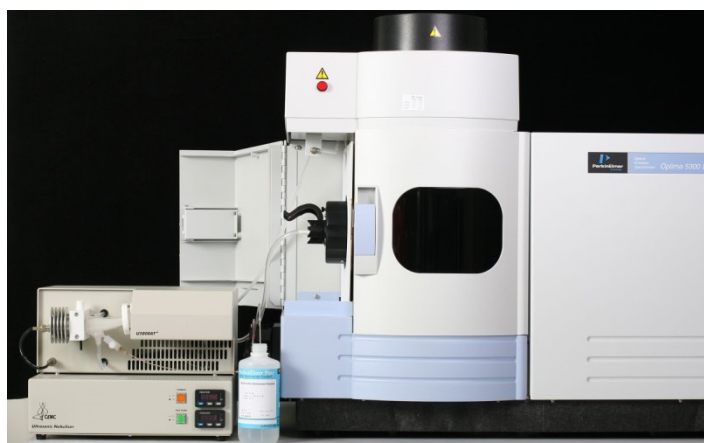
1. One set of calibration standards containing 20, 50, 100, and 200  $\mu\text{g/L}$  Al, As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, Se, Sn, Sr, Zn. Standards were prepared in 0.07M HCl / 0.4%  $H_2O_2$  using precleaned 125-mL low-density polyethylene (LDPE) bottles.
2. One set of calibration standards containing 20, 50, 100, and 200  $\mu\text{g/L}$  B. Standards were prepared in 0.07M HCl / 0.2% D-Mannitol using precleaned 125-mL low-density polyethylene (LDPE) bottles.
3. One set of calibration standards containing 20, 50, 100, and 200  $\mu\text{g/L}$  Hg. Standards were prepared in 0.07M HCl / 0.01% L-Cysteine using precleaned 100-mL borosilicate glass volumetric flasks.

## ICP-AES AND ULTRASONIC NEBULIZER OPERATING PARAMETERS

The standard nebulizer / spray chamber of the ICP-AES instrument was removed. An interface kit (nebulizer gas line and sample out line) was then used to connect the ultrasonic nebulizer to the ICP-AES. Setup time was approximately 5 minutes. Operating parameters are given in Table 1 below.

**Table 1. Operating Parameters**

ICP-AES	PerkinElmer Optima 5300DV
ICP Power	1350 W
Plasma Gas	15 L/min
Auxiliary Gas	0.2 L/min
Nebulizer Gas	0.55 L/min
Resolution	Normal
Viewing	Axial
Points/peak	3
Integration Time	5 sec min, 20 sec max
Replicates	5
Ultrasonic Nebulizer (USN)	Teledyne CETAC U5000AT <sup>+</sup>
USN Sample uptake rate	1.5 mL/min (pumped)
USN Heater temperature	140°C
USN Condenser temperature	3°C



**Figure 4. PerkinElmer 5300DV ICP-AES & Teledyne CETAC U5000AT<sup>+</sup> USN**

## IDLs and LOQs FOR ICP-AES WITH ULTRASONIC NEBULIZATION

Instrument detection limits (IDLs) and limits of quantitation (LOQs) are listed in Table 2 for the regulated elements using the ultrasonic nebulizer (USN) with ICP-AES detection. IDLs are defined as 3 times the standard deviation of the blank concentration; LOQs are defined as 10 times the standard deviation of the blank concentration. Blanks include 0.07M HCl / 0.4% H<sub>2</sub>O<sub>2</sub>, 0.07M HCl / 0.2% D-Mannitol, and 0.07 M HCl / 0.01% L-Cysteine.

**Table 2. IDLs and LOQs for EN-71 Regulated Elements using ICP-AES with Ultrasonic Nebulization**

Element	Wavelength (nm)	IDL (µg/L)	LOQ (µg/L)
Al	396.153	0.08	0.27
As	193.696	0.37	1.25
B	249.772	0.15	0.51
Ba	233.527	0.06	0.19
Cd	228.802	0.02	0.06
Co	238.892	0.02	0.07
Cr	267.716	0.03	0.09
Cu	327.393	0.06	0.19
Hg	194.164	0.16	0.53
Mn	257.610	0.02	0.06
Ni	231.604	0.04	0.15
Pb	220.353	0.10	0.32
Sb	206.836	0.25	0.83
Se	196.026	0.49	1.63
Sn	189.927	0.13	0.42
Sr	460.773	0.04	0.12
Zn	213.857	0.02	0.07

Measured migration levels in mg/kg for the regulated elements in EN-71 Part 3 are given in Table 3. ND = not detected according to numerical data and examination of blank, standard, and sample emission spectra. None of the three toy samples exceeded migration limits for Category III samples.

Table 3. Measured Trace Element Migration Levels in Various Category III Toy Samples

Element	Wavelength (nm)	Migration Limit Cat.III (mg/kg)	Green Plastic Ring (mg/kg)	Fake Moustache Fiber (mg/kg)	Red Paint – Wood Blocks (mg/kg)
Al	396.153	70,000	0.07	18.9	38.6
As	193.696	47	ND	ND	ND
B	249.772	15,000	ND	0.51	1.5
Ba	233.527	18,750	ND	2.2	108
Cd	228.802	17	ND	0.05	0.2
Co	238.892	130	ND	ND	ND
Cr	267.716	460	ND	16.4	0.4
Cu	327.393	7,700	0.04	0.3	1.1
Hg	194.164	94	ND	ND	ND
Mn	257.610	15,000	0.04	0.9	29.6
Ni	231.604	930	ND	0.3	0.7
Pb	220.353	160	ND	0.2	0.5
Sb	206.836	560	ND	0.8	ND
Se	196.026	460	ND	ND	ND
Sn	189.927	180,000	0.07	3.3	35.4
Sr	460.773	56,000	0.1	0.2	60.7
Zn	213.857	46,000	0.08	1.7	12.3

## RESULTS AND DISCUSSION

Using axial-viewing ICP-AES with ultrasonic nebulization, IDLs for the 17 regulated elements are all below 1 µg/L, with a range of 0.02 (Cd, Co, Mn, Zn) to 0.49 (Se) µg/L. Use of D-Mannitol and L-Cysteine enabled excellent calibration of B and Hg, with correlation coefficients of 0.9999 and 0.9998, respectively. Chromium data is reported as total Cr since Cr(III) and Cr(VI) speciation was not performed and can be part of future work. Reported element concentrations in the simulant HCl solution are all well below the EN-71 migration limit for Category III toy materials. Future work can also include Category I (ex. crayons) and Category II (ex. glue sticks) toy items.