Challenge

Validating the safety of children's toys to European Standards

Solution

Determination of toxic elements and species in toy materials by ICP-MS according to EN 71-3

Determination of Trace Elements in Toys

Introduction

The safety of toys and children's products has been regulated within the European Community under European Standard EN 71 for many years and is a harmonized standard under Directive 2009/48/EC. Part 3 of the standard defines the migration of certain elements with the most recent update in 2013 (as EN 71-3: 2013), which supercedes EN 71-3: 1994.

The Toy Safety (EU) Directive contains maximum migration limits for three categories of toy materials (Table 1):

- Category I : Dry, brittle, powder like or pliable materials.
- Category II : Liquid or sticky materials.
- Category III : Scrapped-off materials.

The Standard specifies requirements and test methods for the migration of Al, Sb, As, Ba, B, Cd, Cr (III), Cr (VI), Co, Cu, Pb, Mn, Hg, Ni, Se, Sr, Sn, organotin compounds and Zn from toy materials and from parts of toys.

The migration limits apply to toys that clearly demonstrate a hazard to young children due to sucking, licking, swallowing or prolonged contact with skin. The migration procedure simulates contact of the toy material with gastric juices for a period of time after swallowing.

Table 1: Maximum migration limits from toy materials

Element	Cat. I (mg/kg)	Cat. II (mg/kg)	Cat. III (mg/kg)
Aluminium	5625	1406	70000
Antimony	45	11.3	560
Arsenic	3.8	0.9	47
Barium	1500	375	18750
Boron	1200	300	15000
Cadmium	1.3	0.3	17
Chromium (III)	37.5	9.4	460
Chromium (VI)	0.02	0.005	0.2
Cobalt	10.5	2.6	130
Copper	622.5	156	7700
Lead	13.5	3.4	160
Manganese	1200	300	15000
Mercury	7.5	1.9	94
Nickel	75	18.8	930
Selenium	37.5	9.4	460
Strontium	4500	1125	56000
Tin	15000	3750	180000
Organic Tin	0.9	0.2	12
Zinc	3750	938	46000

The technique of ICP-MS and ICP-OES are preferred in the quantitation of elements in toy materials. The limits also include Cr (III) and the more toxic Cr (VI) forms of chromium and are separated using liquid chromatography (LC) coupled to ICP-MS for detection. The measurement of organic forms of tin is also required with GC-MS being the recommended technique.

Instrumentation

The PlasmaQuant MS was used to demonstrate the excellent detection capabilities of ICP-MS in easily achieving the limits of migration as defined in European Standard EN 71. The instrument operating conditions for the PlasmaQuant MS are specified in Table 2.

The determination of chromium species by LC-ICP-MS is also demonstrated. A low-pressure, ion exchange liquid chromatography system (Elemental Scientific) was utilized to separate both Cr species (CrIII and CrVI). The HPLC operating conditions are specified in Table 3.

Table 2: PlasmaQuant MS operating conditions for migration elements

Parameter	Settings
Plasma Gas Flow	9.0 L/min
Auxiliary Gas Flow	1.05 L/min
Nebulizer Gas Flow	1.00 L/min
iCRC Gas Setting	100 mL/min He
Plasma RF Power	1.30 KW
Dwell Time	20 ms
Scans per Replicate	30 (peak hopping, 1pt/peak)
No. of replicates	3
Pump Rate	10 rpm - black/black PVC pump tubing
Ion Optics	Auto-optimized

Table 3: LC and PlasmaQuant MS operating conditions for Cr speciation

Parameter	Settings
Mobile phase	0.26M Ammonium Nitrate (pH 2)
Flow rate	170µl/ min
Run time	9 min
Column	Anion Exchange
Scan mode	Time Resolved
Dwell time	500 ms
Isotope	^{52}Cr
iCRC Gas Setting	50 mL/min H_2
Ion Optics	Optimized for Cr isotopes

Samples and Reagents

Coatings of paint of various colours (pink, red, green, yellow, blue) were scraped off from 8 different toy parts purchased from two toy stores. One store claimed its shovel, rake and bucket set where made from biologically friendly materials, while a second set from another store claimed to be 'made in China'. The samples were prepared as defined in European Standard EN 71-3 with the following steps taken:

- Approximately 0.5g of paint was accurately weighed and mixed with 25 mL solution of 0.07 mol/L hydrochloric acid.
- The mixture was checked for acidity, stirred for 1h at 37°C and then left unstirred for another hour at 37°C.
- The solution was filtered to separate the paint solids from the solution.
- According to chromium speciation requirements, the samples were neutralized after the migration step using ultrapure ammonia (Merck).

Following preparation, the samples were measured using the PlasmaQuant MS. Recovery tests were also performed by spiking a known amount of each element in all 8 samples.

A separate method was developed for the determination of chromium species in the samples by LC-ICP-MS, as previously described.

Results and Discussion

Table 4 shows the average concentration of each element following the duplicate analyses of 8 toy paint samples. Concentrations represent the amount determined in the original solid paint sample in milligrams per kilogram (mg/kg).

Table 4: Analysis Results of 8 toy paint samples

	^{11}B	^{27}Al	^{52}Cr	^{55}Mn	^{59}Co	^{60}Ni
Red Bio toy sample	1.22	0.066	0.096	0.007	0.00038	0.0053
Yellow Bio toy sample	1.14	0.135	0.146	0.009	0.00048	0.0069
Blue Bio toy sample	0.861	16.0	0.432	0.026	0.00082	0.013
Green Bio toy sample	0.847	0.080	0.099	0.006	0.00043	0.0054
Pink China toy sample	0.791	0.223	0.099	0.016	0.00062	0.0071
Yellow China toy sample	0.801	0.334	0.313	0.032	0.0010	0.012
Blue China toy sample	0.804	0.283	0.530	0.040	0.0020	0.10
Green China toy sample	0.767	0.397	0.132	0.030	0.00078	0.012

	^{65}Cu	^{66}Zn	^{75}As	^{78}Se	^{88}Sr	^{111}Cd
Red Bio toy sample	0.024	0.12	<0.02	<0.03	<0.002	0.0006
Yellow Bio toy sample	0.023	0.24	<0.02	<0.03	<0.002	<0.0003
Blue Bio toy sample	0.004	0.074	<0.02	<0.03	0.0131	<0.0003
Green Bio toy sample	0.012	0.086	<0.02	<0.03	<0.002	<0.0003
Pink China toy sample	0.015	0.15	<0.02	<0.03	0.009	0.0007
Yellow China toy sample	0.016	0.16	<0.02	<0.03	0.010	0.0006
Blue China toy sample	0.022	0.19	<0.02	<0.03	0.009	0.001
Green China toy sample	0.030	0.30	<0.02	<0.03	0.017	0.0006

	^{118}Sn	^{121}Sb	^{137}Ba	^{202}Hg	^{206,7,8}Pb
Red Bio toy sample	0.0017	0.0023	0.40	<0.0015	0.0025
Yellow Bio toy sample	0.0017	0.0035	0.005	<0.0015	0.0030
Blue Bio toy sample	0.0021	0.0029	0.016	<0.0015	0.0079
Green Bio toy sample	0.0019	0.0032	0.021	<0.0015	0.0027
Pink China toy sample	0.0065	0.0044	0.049	<0.0015	0.0078
Yellow China toy sample	0.0042	0.0038	0.045	<0.0015	0.0075
Blue China toy sample	0.0073	0.0046	0.049	<0.0015	0.0079
Green China toy sample	0.0045	0.0040	0.089	<0.0015	0.0324

< values represent 10σ quantitative limit

Samples were spiked with 0.5µg/L Hg and 10µg/L of all other elements (0.025mg/kg and 0.5mg/kg, respectively) and the recovery was determined. Samples were also spiked with 0.1µg/L (0.005mg/kg) Cr(III) for the LC-ICP-MS speciation recovery test.

Table 5 shows the averaged results of the recovery test, along with the Limits of Detection (LOD) obtained (3σ).

Table: 5 Recovery test and LODs

Element	Spiking value (mg/kg)	Measured value (mg/kg)	Recovery (%)	LOD (mg/kg)
^{27}Al	0.5	0.48	96%	0.003
^{121}Sb	0.5	0.47	94%	0.0001
^{75}As	0.5	0.49	98%	0.006
^{137}Ba	0.5	0.49	98%	0.001
^{11}B	0.5	0.46	92%	0.02
^{111}Cd	0.5	0.49	98%	0.0001
^{52}Cr (III)	0.5	0.48	96%	0.0002
^{52}Cr (VI)	0.005	0.004	80%	0.0002
^{59}Co	0.5	0.49	98%	0.00007
^{65}Cu	0.5	0.49	98%	0.001
^{206,7,8}Pb	0.5	0.49	98%	0.00008
^{55}Mn	0.5	0.48	96%	0.0006
^{60}Ni	0.5	0.48	96%	0.0008
^{78}Se	0.5	0.51	102%	0.01
^{88}Sr	0.5	0.50	100%	0.0005
^{118}Sn	0.5	0.48	96%	0.0002
^{66}Zn	0.5	0.47	94%	0.003
^{202}Hg	0.025	0.025	100%	0.0005

Figure 1 displays the overlaid chromatograms for a toy paint sample, both unspiked and spiked with 0.1µg/L (0.005mg/kg) of Cr(III) and Cr(VI).

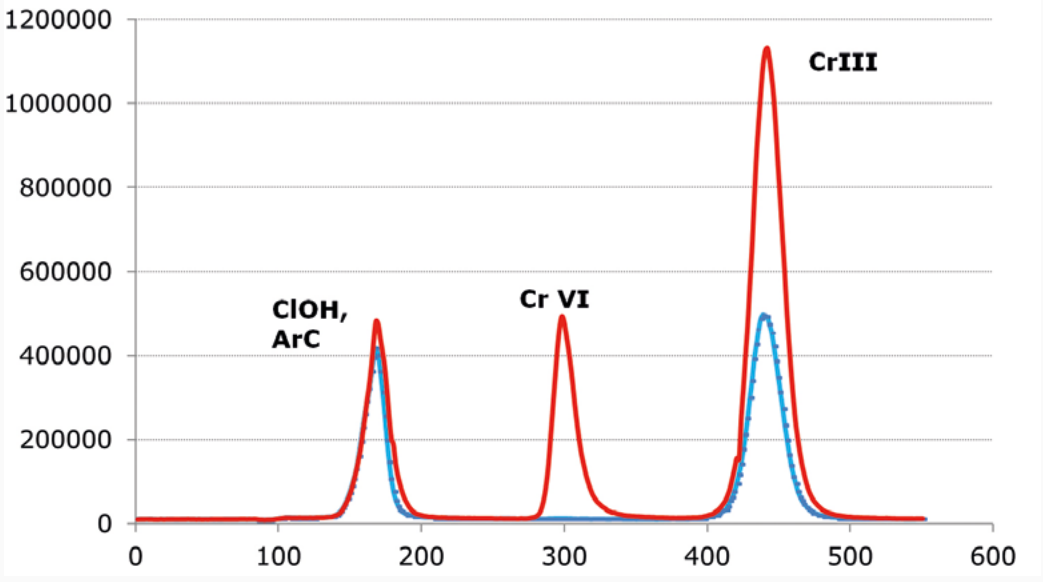

Fig. 1 Chromatograms showing an addition of 0.005 mg/kg (red) of Cr(III) and Cr(VI) on a toy sample (blue)

Conclusion

The PlasmaQuant MS provides a very effective, simple to use solution for the analysis of toy materials according to European Standard EN 71 Part 3.

The addition of Helium collisional gas within the integrated Collision Reaction Cell (iCRC) effectively removes common spectroscopic interferences on important elements including As, Se and Cr. This allows for very low limits of detection to be achieved, easily meeting those defined in the Standard.

The coupling of an ion exchange LC system to the PlasmaQuant MS also offers the ability to separate and quantitate the more toxic hexavalent chromium (CrVI) from the less toxic CrIII to less than 1µg/kg. Well below the maximum migration limit for all three categories.

Headquarters
Analytik Jena GmbH
Konrad-Zuse-Strasse 1
07745 Jena · Germany

Phone +49 3641 77 70
Fax +49 3641 77 9279

info@analytik-jena.com
www.analytik-jena.com

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