

# Analysis of Imported Children's Toys for Heavy Metals



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## ABSTRACT

Over the past decade the regulations regarding potentially hazardous elements and compounds have increased in scope and decreased the restricted compound limits. Children's consumer products have been an active focus for study and regulation due to their ability to expose infants and children to potentially damaging and dangerous chemicals. In regards to organic chemicals, certain phthalates and BPA have been either restricted or banned in children's plastic products. As for inorganic contaminants, there is a recognized list of toxic metals (As, Pb, Hg, Cr, Cd, Sb) that can be found in children's products. The levels and methods of determination of the concentration of these metals can differ between regulatory agencies and countries. The list below shows the most recent limits for heavy metals in children's products.

Regulations	Metal (PPM)						
	As	Ba	Cd	Cr	Hg	Pb	Sb
US ASTM F2853-10 (Paint Layers), F968-8.1 & 8.2 (Metal Content in Toys) & CPSC-CH-E1002-8.2 (Total Pb)	25	1000	75	60	60	90	60
EU EN 71, Part 3 (Migration) & ISO 8024-3	25	1000	75	60	60	90	60

This study looks at the concentration of hazardous inorganic elements detected in imported children's toys by ICP/MS. These toys were previously studied for restricted phthalates and BPA by GC/MS and were found to have high levels of hazardous organic chemicals that were at concentrations at or far exceeding the current US guidelines. This study is a continuation of the examination of these imported toys to determine the inorganic elemental concentration of restricted elemental contaminants.

## MATERIALS

- Dollar Store Toys – subdivided into over 65 samples
  - Paint ground with sample and removed for separate testing
  - Stickers removed
  - Items with oral contact:
    - Whistles
    - Snorkels
    - Baby cup
    - Funny teeth
  - Items with possible oral contact:
    - Army men
    - Rubber duck
    - Doll head
- SPEX CertiPrep Standards:
  - CLMS-1: Multi Element Solution Standard 1
  - CLMS-2: Multi Element Solution Standard 2
  - CLMS-3: Multi Element Solution Standard 3
  - CLMS-4: Multi Element Solution Standard 4
- Reagents:
  - High Purity Nitric Acid
  - High Purity HCl

## SAMPLE PREPARATION

Sample Grinding: SPEX Sample Prep 6970 EFM Freezer/Mill

- General Program
  - 2.5 grams of plastic cut to <5 mm
- Program
  - Precool = 20 minutes
  - Grind for 5 cycles (2 min/cycle)
  - Each cycle = 2 min. cooling
  - Impact rate: 16 impacts/second

Sample Digestion: CEM Mars 5 Microwave with Easy Prep Vessels

- 0.1 g sample with 10 mL HNO<sub>3</sub>
- 15 minute ramp to 210 C and 15 min Hold
- Incomplete digestions of PVC were filtered, dried and reweighed.

Sample Extraction/Migration: CEM Mars 5 Microwave with Easy Prep Vessels

- Based on EN 71, Part 3 (ISO 8124-3)
- Method
  - 1 g sample
  - 10 mL 1 mM HCl
  - 37° C with Stirring for two hours in darkness
- Instrumentation: Agilent ICP-MS 7700
  - Meinhard nebulizer & Cyclonic spray chamber
  - Analysis performed using normal mode: air & collision mode: Helium

### Masses Examined

Element	Gas	Mass Examined
As	Air & He	75
Ba	Air	135, 137, 138
Cd	He	111, 113
Cr	Air & He	52 & 53
Hg	Air	201
Pb	Air	206, 207, 208
Sb	Air	121, 123

### Instrument Conditions

Condition	ICP-MS Agilent 7700
Power	1550 W
Plasma Gas	15 L/min
Aux Gas	0.3 L/min
Nebulizer Gas	0.80 L/min
Sampling rate	0.3 mL/min

## EXPERIMENTAL DESIGN & RESULTS

Samples digested and extracted to determine concentration of metals. Undigested materials in some toys were dried and reweighed.

1. Digestion of toys in first experiment

Regulatory Limit	Metal (PPM)						
	As	Ba	Cd	Cr	Hg	Pb	Sb
Min	0.1	0.4	0	0.28	0.02	0.12	ND
Max	1.7	2000	0.5	10	1	1.8	40
Mean	0.6	553	0.2	3.2	0.29	0.79	2.2

Concentrations in red are higher than regulations allow

2. Stomach acid simulation migration of metals experiment (Two methods cited for calculation in literature)

### A. Dry weight method

- Sample material dried, reweighed & subtracted from initial sample weight = 10 mg (mean)
- Benefit of more accurate weight of sample dissolved
- Increases error in amount recovered

Regulatory Limit	Metal (PPM)						
	As	Ba	Cd	Cr	Hg	Pb	Sb
Duck	6.4	500000	5.2	144	0.31	21	6.5
Sippy Red	2.8	90000	1.6	172	< 1	25	7.4
Ninja Red	4.8	10000	1.8	181	< 1	31	11
Sippy Pink	4.5	2000	3.3	225	1.03	32	32.1
Doll Face	48	3000	2.2	60	< 1	44	3.6
Flute	4.3	2000	1.9	170	< 0.9	44	4.6
Ninja Yellow	4	1000	3.9	1513	< 0.2	61	5.3
Yellow Car	13	40000	3.8	373	< 0.9	102	93.4
Flute Medallion	16	10000	3.3	470	< 0.6	104	4.9
Red Car	18	70000	6.8	447	< 0.3	123	5.3
Silver Seats	66	100000	18	747	< 1	838	269
Doll Dress	79	80000	41	1370	< 0.4	1018	2300

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### B. Net weight method

- Initial sample weight used to calculate concentration
- Our samples = 1 g
- Decreases overall concentrations since amount dissolved not accounted for in calculations

Regulatory Limit	Metal (PPM)						
	As	Ba	Cd	Cr	Hg	Pb	Sb
Duck	0.1	5000	0.1	1	ND	0.21	0.07
Sippy Red	ND	900	ND	2	ND	0.25	0.07
Ninja Red	ND	100	ND	2	ND	0.31	0.11
Sippy Pink	ND	20	ND	2	ND	0.32	0.32
Doll Face	0.5	30	ND	1	ND	0.44	0.04
Flute	ND	20	ND	2	ND	0.44	0.05
Ninja Yellow	ND	10	ND	15	ND	0.61	0.05
Yellow Car	0.1	400	ND	4	ND	1.02	0.93
Flute Medallion	0.2	100	ND	5	ND	1.04	0.05
Red Car	0.2	700	0.1	4	ND	1.23	0.05
Silver Seats	0.7	1000	0.2	7	ND	8.38	2.69
Doll Dress	0.8	800	0.4	14	ND	10.2	23

Concentrations in red are higher than regulations allow

3. Second digestion of selected toys from migration study

Regulatory Limit	Metal (PPM)						
	As	Ba	Cd	Cr	Hg	Pb	Sb
Red Car	ND	376	ND	2	ND	1	0.3
Yellow Car	ND	119	ND	4	ND	6	5.4
Silver Seats	2	290	1	11	ND	23	16
Car Stickers	1	177	ND	17	ND	4	1
Doll Dress	ND	184	ND	7	ND	4	301

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## CONCLUSIONS

### Migration Methods

The migration or extraction methods simulate the actual exposure of the metals in a toy to a child's system but the method that is used to calculate that actual exposure can greatly change the apparent concentration of elements.

- Dry weight calculations take into consideration only the portion of the toy which is dissolved into the gastric fluid.
  - The negative argument for the use of this calculation comes from the increased error in the drying and reweighing of sample materials.
  - Concentrations are greatly increased when calculations are made on the dry weight of the sample.
    - As, Ba, Cd, Cr, Pb, & Sb for toys (e.g. Doll's Dress) greatly exceed limits
    - Cd & Cr levels above limits in all toys using Dry Weight Calculations
- Net weight or total weight calculations do not take into consideration that only a small fraction of samples will be extracted into the gastric fluid.
  - Concentrations are greatly reduced when based on the total weight of sample material.
    - Concentrations of metals were all below limits except for Sb in Dolls dress which still exceeded limits.

### Digestion Studies

Not all of the sample material was digested. Reweighing samples increased some error.

Digestion results:

- Doll's Dress high in Sb (300 ug/g)
- Highest Ba in Duck, Donkey (2000 ug/g)
- High Sb in Snorkel just below limit (40 ug/g)
- Lowest all elements overall Lion

### Comparison of Digestion and Migration/Extraction Studies For Three Toys

Silver Car Seats	Metal (PPM)						
	As	Ba	Cd	Cr	Hg	Pb	Sb
Digestion	1.5	290	0.6	11	0.04	23	16
Migration TW	0.7	1000	0.2	7	ND	8.38	2.69
Migration DW	66	100000	18	747	< 1.0	838	269

Duck	Metal (PPM)						
	As	Ba	Cd	Cr	Hg	Pb	Sb
Digestion	0.4	6	0.1	1.4	0.1	0.4	0.06
Migration TW	0.1	5000	0.1	1.4	ND	0.21	0.07
Migration DW	6.4	500000	5.2	144	0.31	21	6.5

Doll's Dress	Metal (PPM)						
	As	Ba	Cd	Cr	Hg	Pb	Sb
Digestion	0.3	184	0.5	7.4	0.21	3.6	301
Migration TW	0.8	800	0.4	14	ND	10.2	23
Migration DW	79	80000	41	1370	< 0.40	1018	2300

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- Pb levels for all toys were within limits by digestion and total weight migration methods.
- Dry weight migration methods had results above limits for most of the targeted elements.
- The highest elements found overall were Ba & Sb
  - Ba: Duck & Silver Seats
  - Sb: Dress & Snorkel
- TW Migration and Digestion methods were comparable for some elements in this study – Hg, Cd, Cr
- Sb found highest in digestions
- Ba found highest in TW migration study