

## **Multi-technique Quantitative Analysis and Socioeconomic Considerations of Lead, Cadmium, and Arsenic in Children's Toys and Toy Jewelry**

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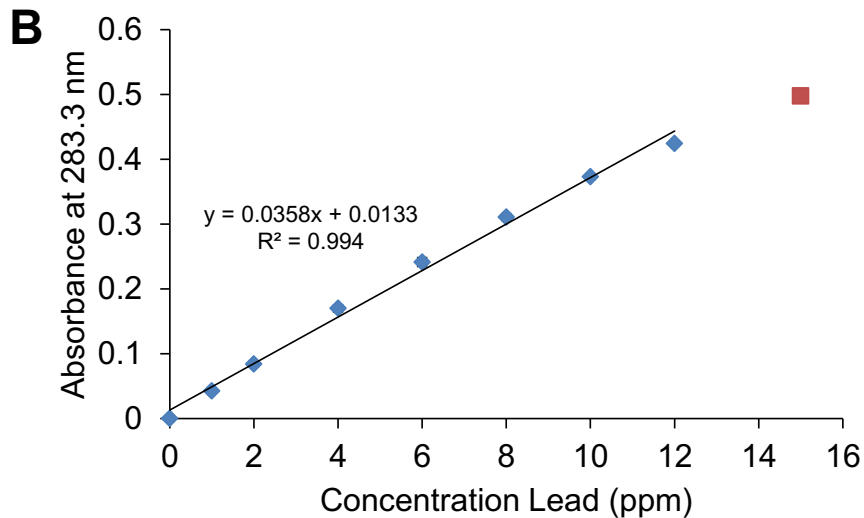
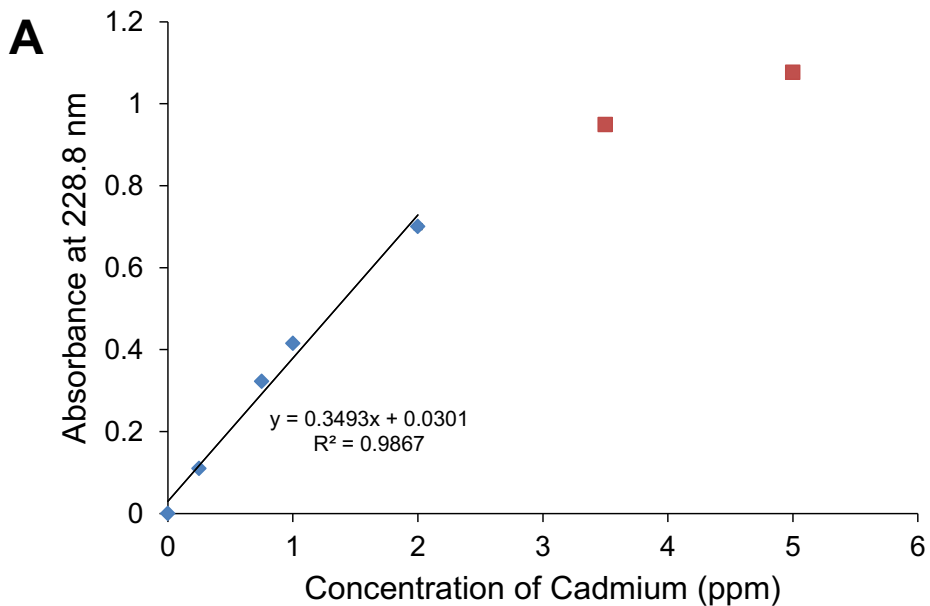
## SM1. Additional Experimental Details

**SM-1.1 *Sampling, Labeling, and Testing.*** Toys/jewelry items were selected without bias to composition, which was assessed during XFS testing, intended use, or gender marketing. Student unaffiliated and with no knowledge of this project were instructed to purchase “children’s toys/toy jewelry” to establish unbiased or “random” selection of items. Because there was no preconceived direction for specific toy composition (e.g., plastic, wood, metal), each sample was identified with a specific five-character sample code. The first digit identifies if it is from a bargain or retail store (B or R). The samples are then categorized by cost (LC or HC). Finally, the last characters identify the type of sample, jewelry or metal, and its makeup, plastic, metal, etc. For example, BLCTM would represent a bargain, low cost, metal toy. In most cases, multiples of each sample were purchased, digested, and analyzed separately and then reported (Table 1 and Table 2) as an average of those analyses ( $n > 1$ ) with corresponding standard error.

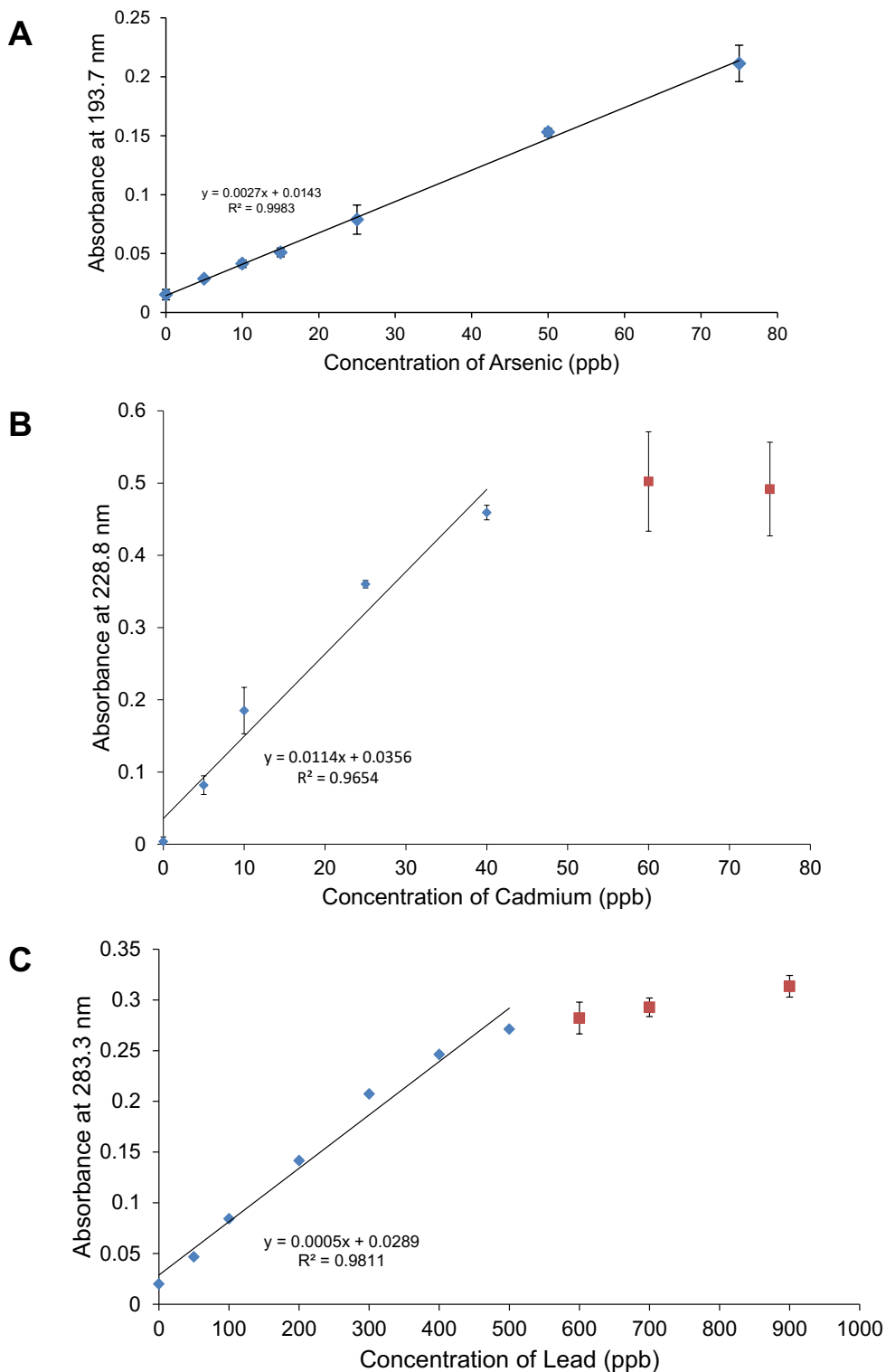
**SM-1.2 *Flame Atomic Absorption Spectrophotometer Details.*** The Varian AA240FS flame atomic absorption spectrophotometer (FL-AAS) featured an air-acetylene flame (13.50/2.00 L/min) and a routinely measured flow rate of  $\sim 0.067$  mL/sec.

**SM-1.3 *Graphite Furnace Atomic Absorption Spectrophotometer Temperature Profile.*** The temperature profile applied to the furnace included preconditioning at a low temperature (85-120°C), ramped to approximately 400°C (1400°C for arsenic) briefly and then extended to a higher range (1800-2600°C). GF-AAS analysis was performed with an autosampler to ensure consistent injections of sample into the furnace.

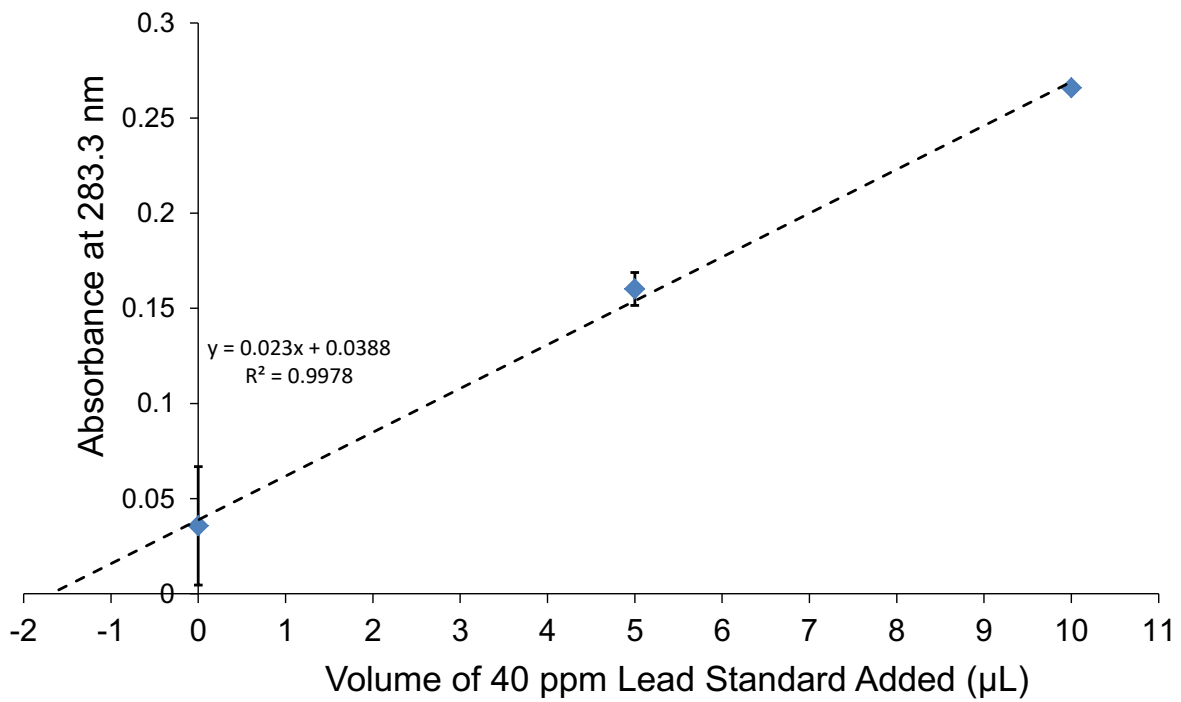
Element	Wavelength (nm)	Lamp Current (mA)
Arsenic	193.7	10.0
Cadmium	228.8	4.0
Lead	283.3	10.0



**Figure SM-1.** Representative examples of calibration curves for (A) cadmium and (B) lead analysis via flame atomic absorption spectroscopy (FL-AAS). Error bars are smaller than the respective markers on the graphs. Linear ranges with regression analysis are depicted with blue diamond markers (◆) and non-linear, dynamic ranges are shown with red square markers (■). Note: Arsenic analysis using FL-AAS is not recommended.



**Figure SM-2.** Representative examples of calibration curves for (A) arsenic, (B) cadmium, and (C) lead analysis via graphite furnace (electrothermal) atomic absorption spectroscopy (GF-AAS). In some cases, error bars are smaller than the respective markers on the graphs. Linear ranges with regression analysis are depicted with blue diamond markers (◆) and non-linear, dynamic ranges are shown with red square markers (■).



**Figure SM-3.** Representative example of a constant volume standard addition analysis using GF-AAS for red beads (Item# )

**Table SM-1. Standard Addition GF-AAS Analysis of CPSC Non-Complaint Toys/Jewelry**

#	Code	Description	Element	GF Reading (mg kg <sup>-1</sup> )	SA – GF (mg kg <sup>-1</sup> )
3	BLCJM-03 <sup>b</sup>	Colorful Metal Rings	Pb	40.8 <sup>†</sup> <sub>±41.2, n=3</sub> (ND-82.4)	227.0 <sub>n=1</sub>
5	BLCJM-05	Silver Chain Charm Necklace	As	177.0 <sub>±86.0, n=3</sub> (109.2-273.7)	164.0 <sub>±58.0, n=2</sub>
6	BLCJM-06 <sup>b</sup>	Painted Metal Hair Clips	As	153.0 <sup>SA</sup> <sub>±199.4, n=2</sub> (11.9-294.0)	191.8 <sub>n=1</sub>
7	BLCJM-07	Gold Chain Charm Necklace	As	95.0 <sub>±74.3, n=3</sub> (10.7-151.1)	106.3 <sub>n=1</sub>
7	BLCJM-07	Gold Chain Charm Necklace	Cd	70.7 <sup>†</sup> <sub>±99.6, n=2</sub> (0.3-141.2)	2181.7 <sub>n=1</sub>
8	BLCJM-08	Yellow Butterfly Earrings	As	82 <sub>±12, n=1, m=2</sub> (73.0 -90.1)	83.7 <sub>n=1</sub>
9	BLCJM-09	Blue Butterfly Earrings	As	111.8 <sub>n=1</sub>	84.3 <sub>n=1</sub>
10	BLCJM-10	Green Butterfly Earrings	As	232.2 <sub>n=1</sub>	140.6 <sub>n=1</sub>
11	BLCJM-11	Metal Charm on Bracelet	Pb	31 <sup>†</sup> <sub>±23, n=1, m=2</sub> (15-47)	545.7 <sub>n=1</sub>
16	BLCJP-01 <sup>b</sup>	Red Celebration Beads	Pb	1124.0 <sub>±1135.4, n=2</sub> (321.2-1926.9)	3180.5 <sub>±1758.4, n=2</sub> (1937.1-4423.9)
17	BLCJP-02 <sup>b</sup>	Black Celebration Beads	Cd	808.1 <sub>±674.3, n=4</sub> (198.7-1771.0)	2400.9 <sub>±2898.5, n=2</sub> (351.3-4450.5)
17	BLCJP-02 <sup>b</sup>	Black Celebration Beads	Pb	2442.2 <sub>±1196.2, n=2</sub> (1363.3-3728.6)	2881.1 <sub>±49.7, n=2</sub> (2548.1-3213.2)
19	BLCJP-04 <sup>b</sup>	Plastic Heart Shaped Bracelets	Pb	143.7 <sub>±155.3, n=2</sub> (33.9-253.5)	5539.3 <sub>n=1</sub>
20	BLCJP-05 <sup>b</sup>	Gemstone Rings - Silver	Pb	87.4 <sup>†</sup> <sub>±153.0, n=4</sub> (ND-316.7)	113.9 <sub>±127.0, n=2</sub> (24.1-203.7)
21	BLCJP-06 <sup>b</sup>	Gemstone Rings - Gold	Pb	191.6 <sub>±155.1, n=3</sub> (45.3-354.3)	118.0 <sub>n=1</sub>
24	BLCJP-09 <sup>b</sup>	Plastic Sapphire Ring	Pb	75.6 <sup>†</sup> <sub>n=1</sub>	1915.8 <sub>n=1</sub>
29	BLCTM-04	Play Handcuffs	As	40.1 <sub>n=1</sub>	23.6 <sub>n=1</sub>
39	BLCTP-03 <sup>b</sup>	Kazoo	Pb	389.6 <sub>±52.9, n=2</sub> (352.1-427.0)	441.0 <sub>n=1</sub>

Notes: <sup>n</sup> indicates the number of different samples of the same toy (replicates); <sup>m</sup> indicates the same sample tested multiple times.

<sup>b</sup> These items' outer coating/paint was digested and analyzed rather than the entire product being digested.

<sup>†</sup> Exceeds regulation on SA-GF AAS but not on GF-AAS

**Table SM-2.** Standard Addition GF-AAS Analysis Confirmation of “Suspect” Toys/ Toy Jewelry from Bargain Stores

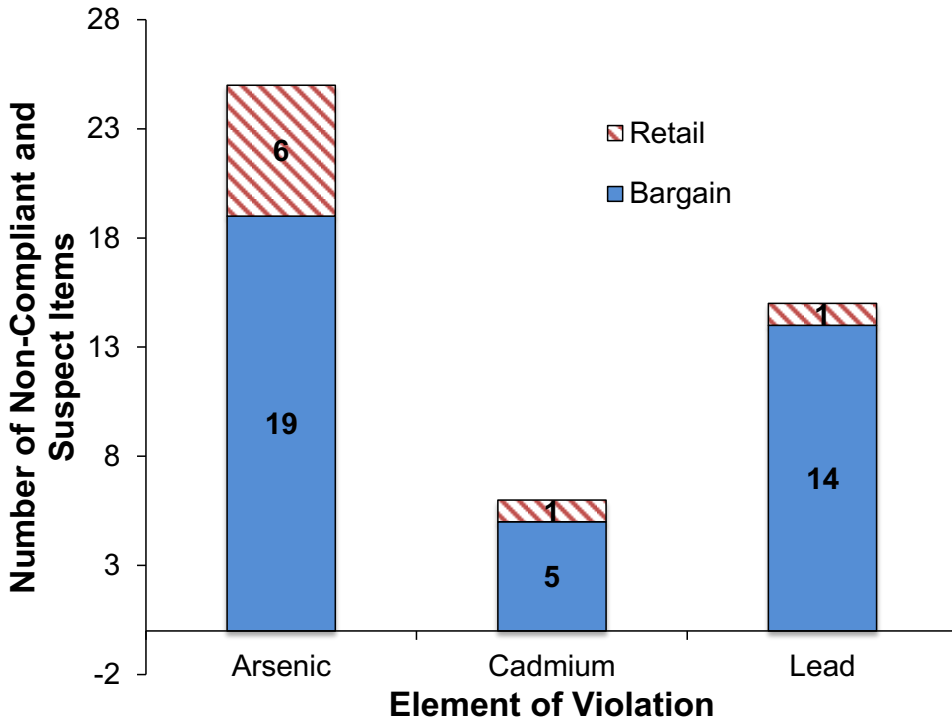
#	Code	Description	Technique	Element	Non-Compliant Reading (mg kg <sup>-1</sup> )	SA – GF (mg kg <sup>-1</sup> )
1	BLCJM-01	Metal Ring with Beads	XFS	As	120.5 <sub>±170.5, n=2</sub> (LOD-241.0)	-
1	BLCJM-01	Metal Ring with Beads	XFS	Pb	801.0 <sub>±410.0, n=2</sub> (511.0-1091.0)	-
11	BLCJM-11	Metal Charm on Bracelet	XFS	As	3253 <sub>±1689, n=3</sub> (1660-5024)	-
11	BLCJM-11	Metal Charm on Bracelet	GF-AAS	Cd	149.4 <sub>±47.2, n=1, m=2</sub> (116.0-182.8)	392.4 <sub>n=1</sub>
13	BLCJM-13	Silver Heart Rings	GF-AAS	As	30.8 <sub>n=1</sub>	29.8 <sub>n=1</sub>
14	BLCJM-14	Metal Charm	XFS	As	2315 <sub>±135, n=1</sub>	-
16	BLCJP-01 <sup>b</sup>	Red Celebration Beads	GF-AAS	As	75.1 <sub>±66.9, n=3</sub> (0.9-130.8)	96.4 <sub>n=1</sub>
16	BLCJP-01 <sup>b</sup>	Red Celebration Beads	GF-AAS	Cd	97.3 <sub>±59.0, n=2</sub> (55.6-139.1)	256.9 <sub>n=1</sub>
17	BLCJP-02 <sup>b</sup>	Black Celebration Beads	GF-AAS	As	176.5 <sub>±263.1, n=3</sub> (49-360.2)	135.2 <sub>±91.5, n=2</sub> (70.46-199.9)
18	BLCJP-03 <sup>b</sup>	Colorful Party Beads Pkg.	FL-AAS	Cd	618 <sub>±681, n=6</sub> (ND-1865)	-
18	BLCJP-03 <sup>b</sup>	Colorful Party Beads Pkg.	XFS	Pb	118.6 <sub>±265.1, n=5</sub> (LOD-592.8)	-
19	BLCJP-04 <sup>b</sup>	Plastic Heart Bracelets	GF-AAS	As	14.1 <sup>†</sup> <sub>±15.2, n=2</sub> (3.4-24.8)	29.7 <sub>n=1</sub>
23	BLCJP-08 <sup>b</sup>	Dollar Sign Ring	XFS	Pb	1568 <sub>±719, n=2</sub> (1059-2076)	-
24	BLCJP-09 <sup>b</sup>	Plastic Sapphire Ring	GF-AAS	As	32.0 <sub>n=1</sub>	38.9 <sub>n=1</sub>
27	BLCTM-02	Gun Key Chain	XFS	As	1954 <sub>±2630, n=1, m=2</sub> (94-3814)	-
28	BLCTM-03	Construction Set	GF-AAS	As	37.5 <sub>n=1</sub>	45.6 <sub>n=1</sub>
43	BLCTP-07 <sup>b</sup>	Gold Medals	GF-AAS	As	33.5 <sub>n=1</sub>	48.5 <sub>n=1</sub>
44	BLCTP-08 <sup>*b</sup>	Play Kitchen Set A	GF-AAS	As	339.3 <sub>n=1</sub>	33.7 <sub>n=1</sub>
44	BLCTP-08 <sup>*b</sup>	Play Kitchen Set A	XFS	Pb	293.8 <sub>±184.5, n=1</sub>	-
45	BLCTP-09 <sup>*b</sup>	Play Kitchen Set B	XFS	Pb	588.6 <sub>±233.3, n=1</sub>	-

Notes: <sup>n</sup> indicates the number of different samples of the same toy (replicates); <sup>m</sup> indicates the same sample tested multiple times.

<sup>b</sup> These items' outer coating/paint was digested and analyzed rather than the entire product being digested.

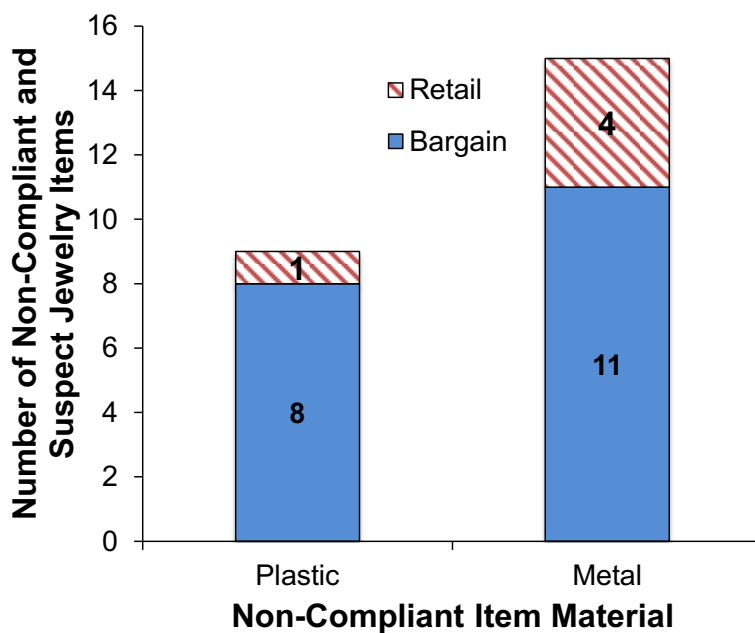
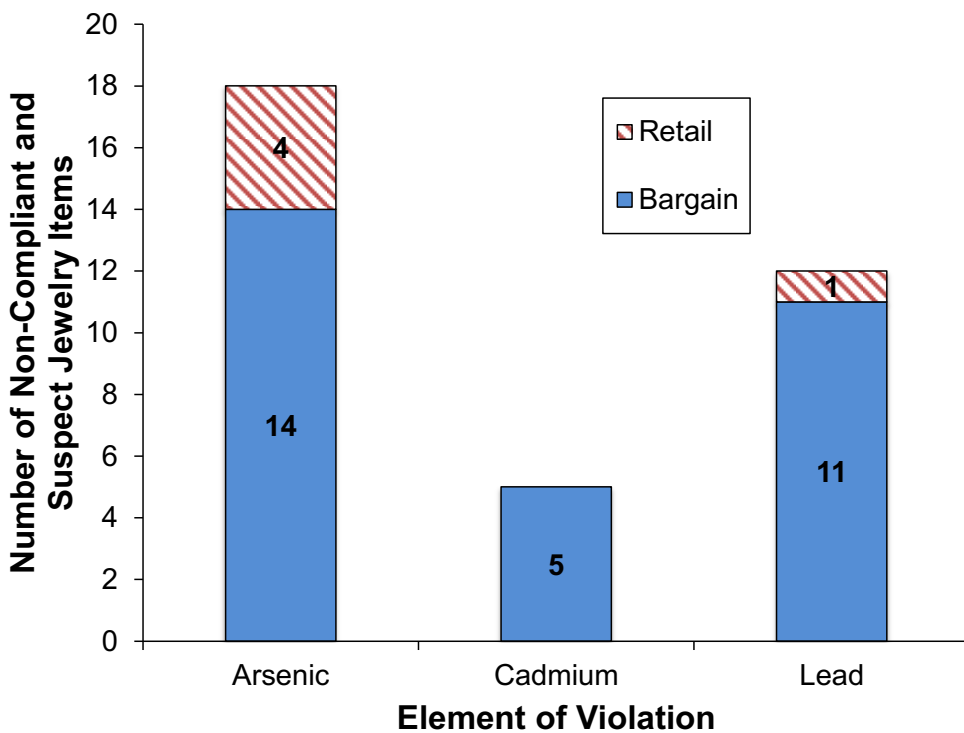
<sup>†</sup> Exceeds regulation on standard addition analysis (AAS-GF) but questionable on AAS-GF.

<sup>\*</sup> Denotes an XFS reading through a selected part of a whole toy.

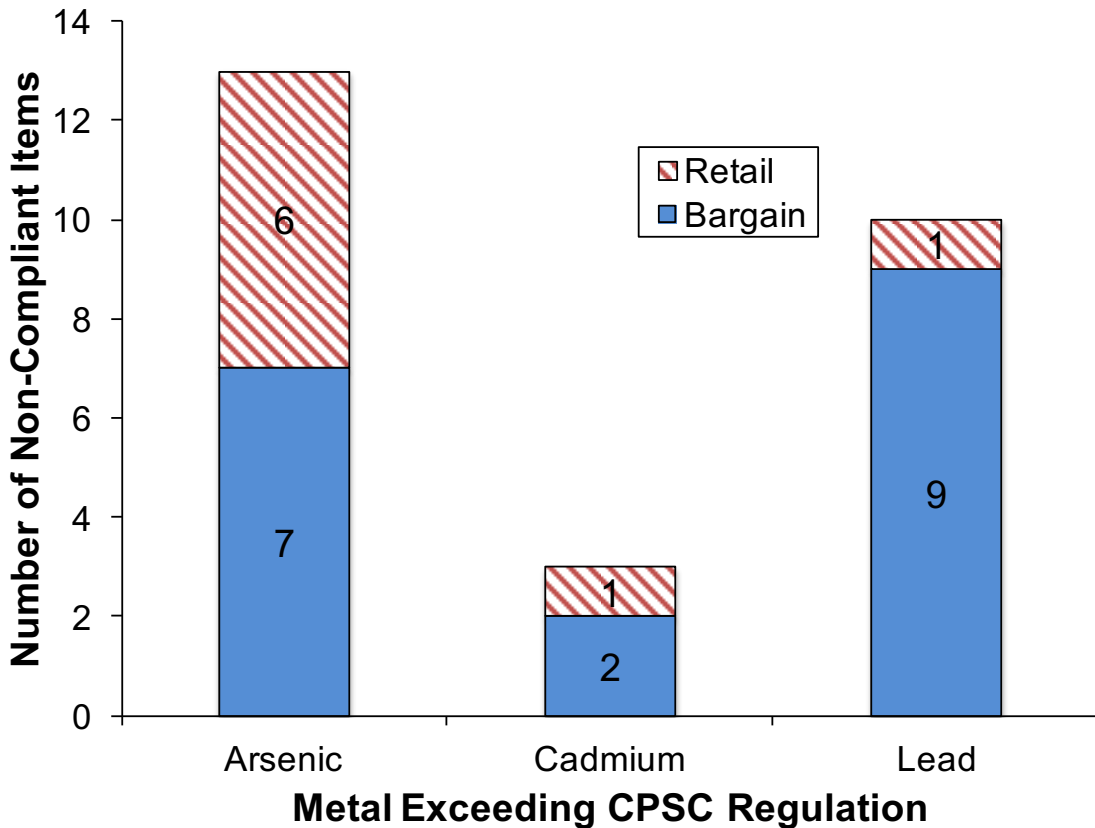


**Figure SM-4.** Non-compliant/suspect item comparison of metal content exceeding CPSC limitation.

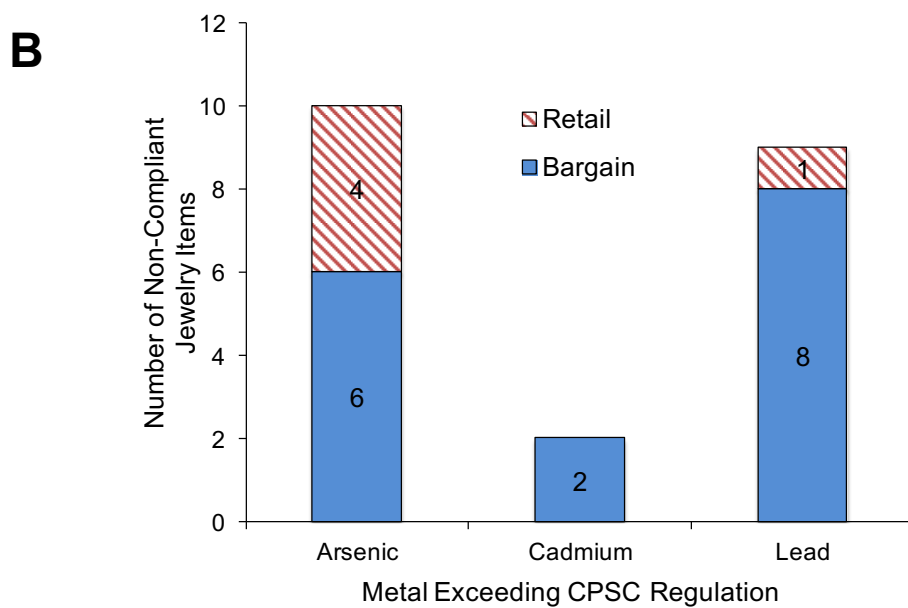
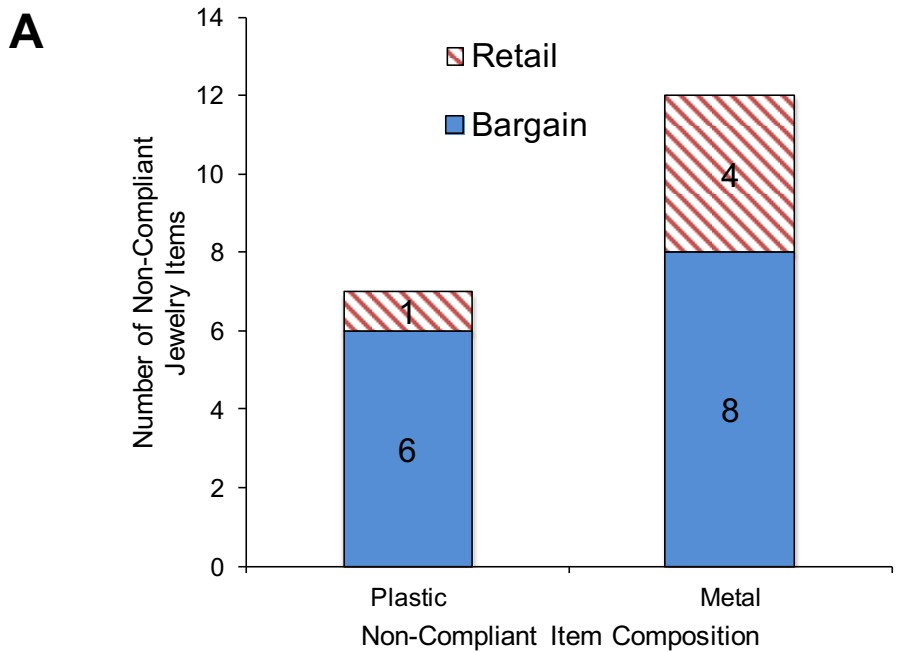


**A****B**

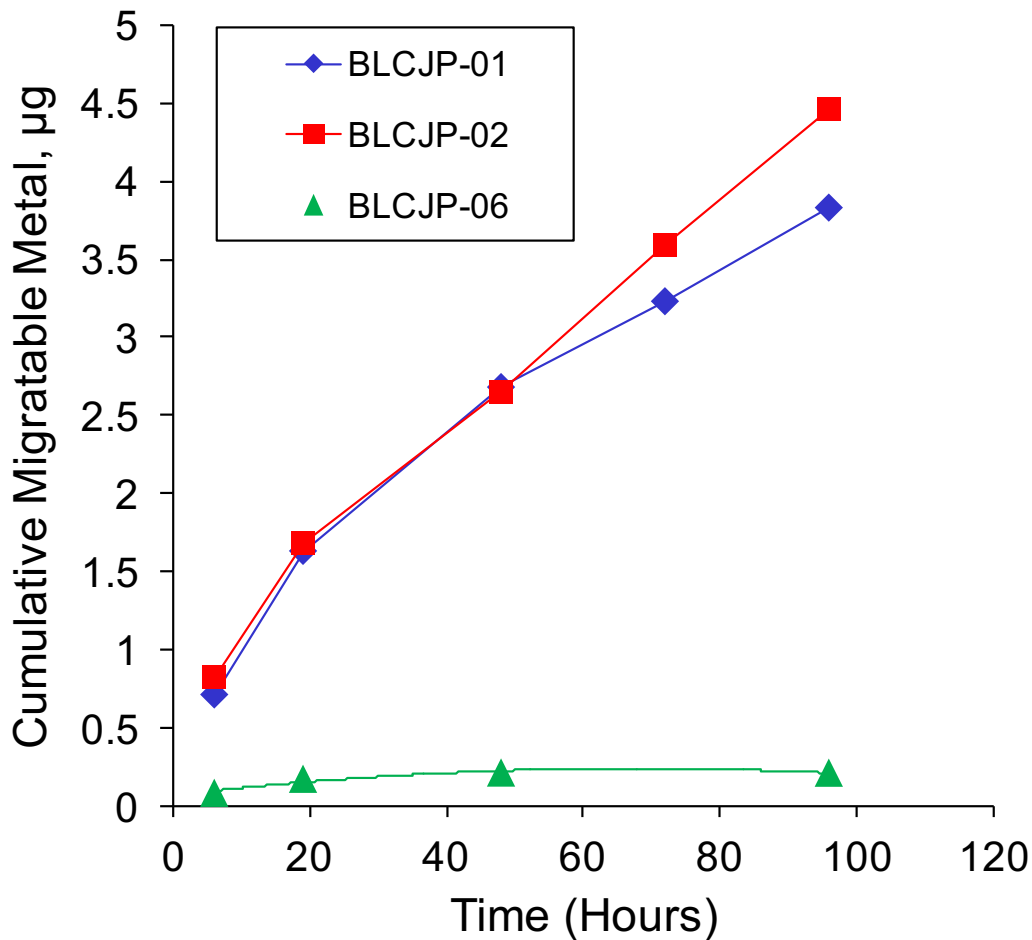
**Figure SM-5.** Characterizations of non-compliant/suspect jewelry items including their (A) composition and (B) metal that exceeding CPSC regulations.



**Figure SM-6.** Non-compliant item comparison of metal content exceeding CPSC limitation with assumption that “suspect” retail items identified only with XFS are actually *non-compliant*. In comparing collective results from product analysis of bargain stores versus retail stores, several key findings are supported. First, the rate of non-compliant toys/toy jewelry from bargain stores (35%) is nearly double that of items purchased at large retail stores (15%). This finding indicates that the type of store from which these products are purchased may be a significant factor in public exposure. Secondly, bargain and retail stores differed significantly in which of the three targeted metals products were found. Of the non-compliant toys/toy jewelry from bargain stores 56% were in violation of CPSC limitation for lead, whereas only 17% of non-compliant items from retail stores showed excessive lead content; the bulk of non-compliant items (86%) surpassing arsenic limits instead. It is evident from the results that jewelry items, as opposed to toys, are much more likely to have metal concentrations that exceed CSPC limits, and therefore represent a greater threat to children who might accidentally ingest them. Nearly 83% (19 of 23) of the total number of samples found to exceed limits, regardless of purchase origin, were classified as children’s jewelry. Metallic-based jewelry (12 of 19, 63%) was more problematic than plastic jewelry (7 of 19, 37%).



**Figure SM-7.** Characterizations of non-compliant jewelry items including their (A) composition and (B) metal exceeding CPSC regulations with assumption that “suspect” retail items identified only with XFS are non-compliant.



**Figure SM-8.** Bioavailability study of select non-compliant bargain items monitoring cumulative mass of migratable or leachable lead over time. Note: Items BLCJP-01 and BLCJP-02 showed an approximate average leachable amount of lead of 0.04 µg/hr.