Quantitative Analysis of Heavy Metals in Children's Toys and Jewelry: A Multi-Instrument, Multitechnique Exercise in Analytical Chemistry and Public Health

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Ⓢ *Supporting Information*

ABSTRACT: For most chemistry curricula, laboratory-based activities in quantitative and instrumental analysis continue to be an important aspect of student development/training, one that can be more effective if conceptual understanding is delivered through an inquiry-based process relating the material to relevant issues of public interest and student career trajectories. Laboratory experiences that actively engage students in this manner can be difficult to identify and execute. A special topics, project-based laboratory module is presented here that utilizes multiple techniques and instruments to investigate toxic metal content (lead, cadmium, and arsenic) in children's toys and toy jewelry. The module effectively illustrates a considerable number of fundamental and advanced quantitative analysis principles including sample digestion, Beer−Lambert law, calibration curve, and standard addition analyses, as well as instrumental analysis considerations of atomic absorption spectroscopy including atomization efficiency (e.g., flames vs furnaces), matrix modifiers, and nondestructive spectroscopy. Module effectiveness stems from the illustration of critical chemical analysis principles in the context of projects with student-directed hypotheses and experimental results that are clearly relevant to the interface of basic science, medicine, and public health: primary career interests for a significant number of undergraduates in the physical and life sciences.

KEYWORDS: *Upper-Division Undergraduate, Analytical Chemistry, Inquiry-Based/Discovery Learning, Atomic Spectroscopy, Quantitative Analysis*

■ INTRODUCTION

Exposure to heavy metals from consumer products can have adverse health effects and is particularly dangerous and damaging to the physical and mental development of children. Heavy metal contamination that has been identified as dangerous by the Occupational Safety and Health Administration (OSHA) includes, for example, arsenic, beryllium, cadmium, hexavalent chromium, lead, and mercury. As human exposure to these particular metals increases, the severity of the adverse side effects consequently increases as well.[1]

Children under the age of six are in a critical developmental stage both physically and cognitively. Due to the persistent mouthing behavior of children in this age group, there is significant risk for heavy metal exposure from contaminated consumer products such as children's toys.[2] Continual exposure to heavy metal toxins through ingestion during mouthing can have serious health effects because of the accumulation of metal in the body. The combination of toxic metals in certain children's toys/toy jewelry, along with the accessibility of these toys to children, and children's developmental vulnerability has been identified as a "risk triangle" by the Intergovernmental Forum on Chemical Safety and highlights a significant public health issue.[2]

Of the heavy metals found in consumer products, arsenic, cadmium, and lead are known to adversely affect mental and physical health with prolonged exposure. Some manufacturers are using arsenic, cadmium, and lead in their toy products for a variety of reasons. Lead, for example, can be used in toys/toy jewelry as a stabilizer, color enhancer, or anticorrosive agent.[3] Cadmium can be used in the production of similar products as a substitute for lead-based stabilizers or to make a product look/feel more realistic, such as enhancing the mass and luster of children's novelty jewelry.[3] The motivation for using arsenic in products is currently unclear, but is suspected to be related to the use of certain coloring dyes.[3]

The United States, along with many other countries, have enacted regulations to prohibit an excess amount of heavy metals in consumer products, including children's toys and toy jewelry items. In 2009, the United States Consumer Product Safety Commission (CPSC) created its first legal statute for the contamination of children's products with lead at 300 mg/kg.[4] Regulatory metal limits continued to be scrutinized in following years as the European Union and International Standards Organization became more stringent on the existence of heavy

metals in children's products. In 2012, the CPSC adopted the American Standards for Testing and Materials (ASTM) standard for toy safety, F963-11.[4,5] This regulation put the United States' regulations on toy safety regarding heavy metal contamination on par with those of other leading nations, including the European Union (EN71 Part 3), Canada (SOR/011-17), and Australia (AS/NZ ISO 8124 Part 3). The current CPSC regulation limits for this country are set at 25 mg/kg As, 75 mg/kg Cd, and 90 mg/kg Pb.[6]

Several quantitative analysis studies have specifically addressed the heavy metal contamination of children's toys/toy jewelry.[3,7−9] Weidenhamer and co-workers, for example, used atomic absorption spectroscopy (AAS) and X-ray fluorescence spectroscopy (XFS) to examine the lead or cadmium content in low cost metallic and plastic jewelry, finding many products in excess of legal limits, as well as having jewelry items with average lead levels between 30 and 44% of the items' weight.[8,9] More recently, Zagury[7] and Leopold[3] researchers performed more expansive testing of a wider range and composition of children's toys/toy jewelry, including screening for arsenic, lead, and cadmium. While both of the latter studies addressed aspects of bioaccessibility, the primary focus of Zagury et al. was a wide range of potential toxins in numerous products[7] while Leopold et al. specifically examined the effectiveness of multitechnique analysis and the socioeconomic implications and factors within the findings.[3] Taken collectively, these studies solidified an overall consensus that numerous toy products are noncompliant, exceeding regulatory levels of these metals.

Our recent study involving multimetal analysis of children's toys/toy jewelry using multiple analytical techniques and instruments illustrates a unique and relevant laboratory project that is rich in both quantitative science and public health education.[3] Other educationally based studies have employed atomic absorption spectroscopy for lead and cadmium analysis, including Brouwer's experiment for analyzing PVC in toys for the metals[10] and Weidenhamer's analysis of lead in circuit boards for nonscience majors.[11] Few of the other studies we have encountered of this nature, however, encompass such a breadth of important quantitative analytical chemistry concepts while also addressing a serious public health issue that relates to a range of students that include those pursuing a career in the sciences (B.S., M.S., Ph.D.) as well as premedical (M.D.) and public health (M.P.H.) oriented students.

In the last year alone, 48,014 applicants completed on average 14 applications to medical schools across the country. Of the applicants, a disproportionate number of them (∼65%) of them are applying to medical schools as science, technology, engineering, and math (STEM) majors with a significant number (4966 or ∼16%) of that group applying from physical sciences, including chemistry and physics.[12] Additionally, it is estimated that there are over three hundred institutions that offer a graduate degree in public health also drawing from STEM disciplines.[13] In the upcoming decade, employment opportunities in various public health and medical fields are projected to grow significantly here in the United States in response to implementation of the Affordable Care Act as well internationally with emerging global health issues.[14] Within the field of chemistry, premedical or prepublic health chemistry majors may not find the more classical training in quantitative chemical analysis relevant to their perceived career paths. A quantitative analysis project that analyzes children's toys for toxic metals exposes these students to a very real interface of

science and public health: a project that allows them significant ownership of an idea because there is freedom to examine a number of different toy aspects (e.g., composition, cost, origin of purchase) as well as a variety of public health implications (e.g., healthcare, socioeconomic factors, store/distributor location) while still encompassing a large number of basic analytical skills and more advanced analysis. Within this project the conceptual and practical lessons range from basic techniques of sample digestion, ppm vs ppb concentrations, dilution procedures, and pipetting as well as traditional methodology of sample analysis using calibration curves and standard addition. More advanced analytical concepts are also accessible within the project, including the difference between spectroscopic instrumentation, most notably atomization efficiency between flame (FL) and graphite furnace (GF) AAS with or without chemical additives.

■ DESIGN/IMPLEMENTATION OF QUANTITATIVE ANALYSIS MODULE

The educational goals of this project module include independent student learning and practice of a number of fundamental quantitative/instrumental analysis techniques and concepts in the context of an interesting, public health related research experience. The numerous aspects of testing toys/toy jewelry (e.g., composition, price, location, product lots, etc.) allow for students to form their own hypotheses or questions: an important aspect of an effective project experience. For this paper, two undergraduate (sophomore and junior) biochemistry majors enrolled in an independent study to perform quantitative analysis of lead, cadmium, and arsenic in children's toys and toy jewelry from bargain stores using atomic and fluorescence spectroscopies. Both students were initially trained by the instructor in quantitative chemical analysis techniques, equipment, and instrumentation (see below for more detail). Neither student had significant, prior quantitative analysis training, nor does the biochemistry major require students to take quantitative analysis. After initial training, the students were charged with hypothesis development, sample selection, record keeping, and digestion/analysis of samples. The students ultimately devised the hypothesis of comparing a large number of inexpensive toys from bargain/discount stores to similar toys purchased at major retail chains (results are published elsewhere[3]). During the course of the semester, the students worked once a week for 4 h over 3−4 weeks, each 3−4 week segment starting from new sample digestions and culminating in spectroscopic measurement of metal content in the products. As will be described, the repetition of the digestion to analysis cycle is conducive to student's schedules and is essentially required because calibration curves have to be regenerated on a regular basis to accommodate for changes in the instrumentation. The process was continually repeated and the procedures honed over two semesters and two summers until 100 toys/toy jewelry items had been tested[3] and the detailed procedures for the 3−4 week implementation had been fully developed.

Depending on the specific institution's available resources, the project module can be implemented in a number of ways: as part of a course, as an independent project, within the scope of undergraduate research, or within a special topics course on quantitative analysis or public health science. After initial training in quantitative analysis techniques/equipment/instrumentation, the module described herein requires approximately three 4 h laboratory periods to generate significant results that illustrate a meaningful, hypothesis-driven comparison, partic-

Table 1. Selected Averages of Metal Concentrations from a Multitechnique/Multi-Instrument Analysis of Lead, Cadmium, and Arsenic in Children's Toys and Toy Jewelry[a]

Sample Description	Metal	CPSC Regulatory Limit (ppm)	Calibration Curve (ppm)		Standard Addition GF-AAS (ppm)	XFS Analysis (ppm)
			FL-AAS	GF-AAS		
Black celebration beads	Pb	90	3288	2442	2881	3346
	283.3 nm		($\pm$3983, $n = 4$)	($\pm$1196, $n = 2$)	($\pm$50, $n = 2$)	($\pm$2459, $n = 3$)
Colorful metal rings	Pb	90	ND	41	227	130
	283.3 nm		$n = 2$	($\pm$41, $n = 3$)	$n = 1$	($\pm$112.4 $n = 3$)
Gold chain charm necklace	Cd	75	13	71	2182	2317
	228.8 nm		($\pm$18, $n = 2$)	($\pm$99, $n = 2$)	$n = 1$	($\pm$2416, $n = 3$)
Gold chain charm necklace	As	25	N/A	95	106.3	3372
	193.7 nm			($\pm$74, $n = 3$)	$n = 1$	($\pm$970, $n = 3$)

[a]Notes: CPSC = Consumer Product Safety Commission regulatory limit; ND = nondeterminable; n = number of replicates. Uncertainty is standard error. Significant variability for sample measurements by individual techniques is common in this type of study and is likely related to differences in manufacturing lots of the products and opportunistic use of raw materials by foreign manufacturers.[3,7] In addition, variations between the different instrumental analyses and techniques is likely due to their inherent differences such as atomization efficiency (FL-AAS vs GF-AAS) or matrix effects (calibration curve vs standard addition), for example.

ularly if an entire class performs the module as a group. Our suggestion is that the module be executed as part of an independent project phase in the context of traditional quantitative/instrumental analysis chemistry courses/laboratories. As such, we have provided a suggested schedule and laboratory documentation (e.g., Instructor's Notes, Student Instructions, Excel templates, example data/results) for this type of implementation, including details of essential topics that should be taught prior to the onset of the project. While the presented project is challenging, there is significant flexibility in terms of the type of analysis and number of instruments/ techniques applied, making it an extremely versatile and adaptable template. The outcomes of this activity range from increased student engagement to dissemination of results in the form of poster presentations at local/regional meetings/ symposia and, in some cases, depending on implementation, writing and publication of results.[3] In particular, independent problem solving skills are enhanced with this project. Indeed, the students performing this work identified it as one of the most meaningful and educational endeavors of their undergraduate careers, largely because they were able to apply their knowledge and demonstrate ownership over the direction and success of the project.

■ EXPERIMENTS

Sample Selection

In an attempt to allow each student to feel ownership of the project, we suggest allowing the students to select their own samples from a bargain/retail store based on a prearranged plan or hypothesis that is developed with the instructor. For best results, it is recommended that the samples all come from those that can be classified as "low cost children's toys/toy jewelry item" with an exterior painted coating. Additionally, variability in individual product measurements can be drastically reduced if extra care is taken to purchase replicate samples of a product from the same manufacturing lot, a challenging feat at times. Examples of different types of studies within this category include comparing items composed of different substances (plastic, metal, etc.) or items from different product bulk lots, or comparing manufacturing countries (e.g., "Made in USA" vs "Made in China"). Regardless of the hypothesis, students should keep a record of each sample's attributes (size, number, color, etc.) and origination store/manufacturer. With so many

possible characterization factors with these samples, it is helpful to identify each toy/toy jewelry item with a sample code that easily characterizes the sample (see Instructor's Notes in Supporting Information for an example). Prior to digestion, each sample's mass should be recorded.

Nitric Acid Digestion and Analysis

The sample should be placed in an acid-washed beaker and carefully immersed in high purity concentrated nitric acid to begin sample digestion. To aid this process, sample digestion solutions can be agitated by hand or using a magnetic stirrer. After the coating has been removed or sample has fully digested (this is dependent on the makeup of the toy, i.e., plastic or metal; please see Instructor's Notes in Supporting Information), the solution and the rinsing of the digestion vessel are gravity filtered into a volumetric flask, and the resulting mixture is then diluted to the marked volume with water. The remaining sample (undissolved solid) is rinsed and placed in a drying oven to remove any excess liquid. Once the sample is completely dried, a final mass by difference is recorded. The mass difference (i.e., before and after digestion masses) represents the amount of sample that was successfully digested and will be subsequently analyzed for metal content. Ultimately, this will allow the metal concentration in ppm in solution, as determined by the Beer−Lambert law, to be converted into mg of metal per kg of sample.

The metal concentrations of the filtered sample solutions should be determined via atomic absorption spectroscopy (AAS) and calibration curve analysis. Each sample should first be tested using the flame atomic absorption spectrophotometer (FL-AAS) to screen for ppm levels of metal(s) concentration. If a sample does not show a ppm concentration of heavy metal using FL-AAS analysis, the sample can then be analyzed using the graphite furnace atomic absorption spectrophotometer (GF-AAS) by first diluting the sample to the ppb range. Dilution of the samples is important especially if the FL-AAS indicated a high level of contamination that would potentially poison the graphite tube with memory effects and damage the instrument. To avoid overconcentrated or highly contaminated samples being deposited in the graphite tube, it is suggested that the student begin with a large dilution (i.e., 1:500 or 1:100), analyze the diluted sample using GF-AAS, and work toward smaller dilutions (1:10 or 1:2) if a signal is not observed.

Calibration Curve Analysis of Samples (Beer−Lambert Law)

Prior to analyzing the sample solutions with AAS, calibration curves need to be constructed for each metal on both FL-AAS and GF-AAS. Standardized metal solutions of increasing concentrations are created based on the expected linear range of each analyte, information that can usually be found in many of the handbooks, manuals, and Web sites associated with the common AAS vendors (e.g., Varian, PerkinElmer). For FL-AAS, the expected linear ranges for lead and cadmium are zero (i.e., blank) to 12 ppm and zero to 5 ppm, respectively. According to standard methods,[15] arsenic requires a higher level of atomization and was not tested using FL-AAS (see Table 1). These standardized solutions are created in volumetric flasks from 1000 ppm stock metal solutions and diluted with ultrapure water (see Instructor's Notes, Supporting Information, for example preparation). Multiple replicates of each standard should be made to encompass measurement and instrument variability. Blank measurements as well as known standard samples in nitric acid should be routinely checked against the working calibration curve as a quality control to indicate if a new calibration curve should be generated, an especially important aspect of experiments that are ongoing over the course of weeks. An example of a calibration curve and linear regression analysis for lead using FL-AAS is shown in Figure 1A. Sample calibration curve data for both the flame and furnace AAS for lead, cadmium, and arsenic are provided as part of the Supporting Information. After acceptable calibration

curves have been established and subsequent best fit linear regression analysis has been performed, the absorbance of the sample digest should be measured to determine the ppm concentration of the metal in the sample digest solution.

If the samples do not contain ppm metal concentrations, a similar procedure is used to prepare a calibration curve for GF-AAS analysis, a technique with ppb detection capability. Standards for the furnace should be created in a similar manner to those above. The concentration ranges will be much lower, however, and may require a new stock solution to be made. Standard concentration ranges for As, Cd, and Pb are 0−75 ppb, 0−40 ppb, and 0−400 ppb, respectively. It should also be noted that the furnace requires a much smaller volume of sample during analysis, allowing standards to be made in 25 mL volumetric flasks. Arsenic analysis using GF-AAS is aided greatly with the addition of $Ni(NO_3)_2$, a chemical additive, matrix modifier that was added to all arsenic standards and samples.[15]

Standard Addition Analysis (Matrix Compensation)

Because many of the children's toy/toy jewelry samples have complex matrices, standard addition analysis provides an effective method for more accurate metal concentration determination. Standard addition analysis using GF-AAS is conducted on the samples identified as contaminated (non-compliant) through calibration curve analysis. For each of these samples, 4−5 solutions are created from the sample's original digestion solution in 2 mL volumetric flasks with successive additions of standard metal solution. Standard solutions are added to these flasks so that the absorbance of the final solution is 1.5 to 3 times that of the original sample digest (i.e., no standard added).[16] All of the flasks are diluted to volume. While the volume of added stock solution (of known concentration) will increase incrementally, the final volume (2 mL) remains constant. These solutions should then be analyzed using GF-AAS.

X-ray Fluorescence Spectroscopy Analysis

If possible, students should confirm spectroscopic results using an XRF analyzer. The correct analysis setting should be selected on the analyzer based on the composition of the toy (metal, plastic, etc.). The analyzer is then held to an undigested sample for a minimum of 60 s, and the displayed results are imported to another device or recorded.

Data Analysis

As previously indicated, FL-AAS or GF-AAS analysis of sample digest will yield solution metal concentrations of ppm and ppb, respectively. These concentrations are then translated to the total mass of metal in the sample. By weighing the toy sample before and after metal digestion of the coating, for example, the total metal content of the item can be reported as mg of metal/kg of toy (ppm) or μg of metal/kg of toy (ppb). It is these values that are compared to government regulations for compliance.[4,5,17]

Figure 1. Lead calibration curves generated from the analysis of lead standard solutions using (A) FL-AAS and (B) GF-AAS. Linear regression analysis for the "best fit straight line" in both graphs used to determine the concentration of lead in toy and toy jewelry sample digests. In some cases, standard deviation error bars are smaller than markers for average absorbance ($n = 3–5$).

■ HAZARDS

Concentrated nitric acid is extremely dangerous. Sample digestion should be conducted in fume hoods with appropriate personal protective equipment (e.g., lab coat/apron, gloves, and eye protection). Watch glasses may be used to cover particularly violent digestion reactions for both safety and prevention of sample loss. As with any strong acid, caution should be employed when capping, adding water to, or mixing the flasks.
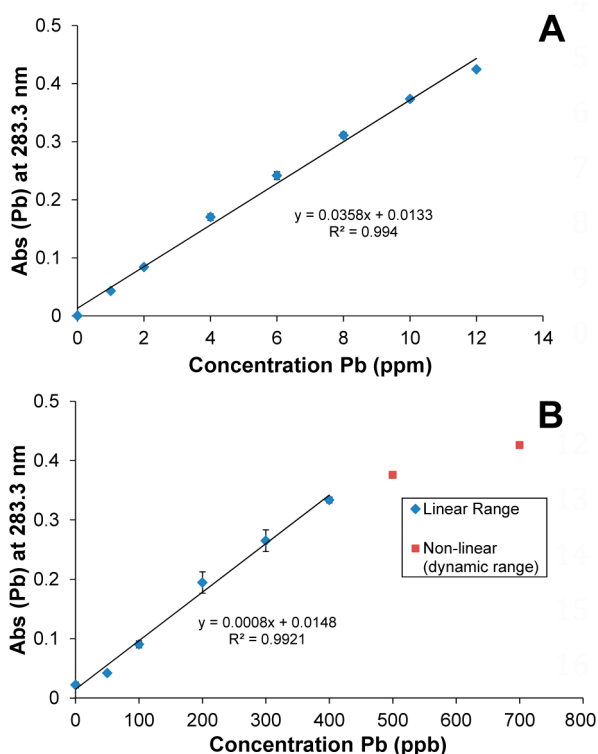
■ RESULTS AND DISCUSSION

Using the experiments described above, analysis of nearly 100 children's toys and toy jewelry was performed by two undergraduates as a project experience within our chemistry curriculum.[3] It is envisioned that this type of study could be part of a lab project sequence within traditional quantitative and instrumental training of chemistry and biochemistry majors.

Calibration Curve Analysis

Figure 1 illustrates a calibration curve used for the FL-AAS analysis of lead in toys at ppm levels. Few of the items tested were found to contain ppm levels of metal contamination unless it was a predominantly metallic object that was completely digested.[3] More often, the analysis of paint and coatings from the toys/toy jewelry items were determined to have noncompliant levels of lead, cadmium, or arsenic at ppb levels after being tested on the GF-AAS. Figure 1B shows a typical lead calibration curve generated from standard solutions (ppb) and absorbance measured using GF-AAS. Linear regression analysis provides the best fit straight line through the data in accordance with the Beer−Lambert law and is used to determine the concentration of lead in sample toy digests. The concentration of metal in the digest was then used to determine the concentration per gram of the toy or toy coating, which was subsequently compared to regulatory limits. Similar calibration curves could be generated for cadmium and arsenic (see Supporting Information). The obvious difference in sensitivity between the two instruments allows students to consider atomization efficiency factors in each instrument, a major theme of teaching AAS.

Calibration Curve Analysis Using Matrix Modifiers

The analysis of arsenic using GF-AAS allows students to consider the benefit of matrix modifiers, the most common examples covered in quantitative analysis courses being releasing agents and ionization suppressors to combat chemical and ionization interference, respectively.[16,18] Because of arsenic's volatility, the analysis of arsenic requires a stabilizing or protective agent ($Ni(NO_3)_2$) to be used to form stable but volatile complexes with arsenic. Complexation with $Ni(NO_3)_2$ allows for increased atomization efficiency and, ultimately, the sensitivity of the technique by extending the resident time of the analyte within the source light traversing the graphite furnace tube.[15] GF-AAS analysis for arsenic in our samples was preceded with creating standards and samples containing 50 ppm of $Ni(NO_3)_2$. Addition of the matrix modifier has a significant effect on the calibration curves as shown in Figure 2, including higher sensitivity, greater linearity, and lower measurement variability.

Standard Addition Analysis

The matrix complexity of some of the toy/toy jewelry digests makes these samples excellent candidates for standard addition analysis, a superior matrix matching technique.[16,18] In this case, standard addition analysis was used to confirm the non-compliant levels of a metal with the assumption of matrix matched samples. Starting with the sample digest, standard solution spikes were added to the sample to create constant volume standard addition plots such as the one provided in Figure 3. Linear regression analysis of the data reports an equation of a straight line whose x-intercept is then used to calculate the metal concentration in the original solution (i.e., the sample digest without any added standard). The plot shown in Figure 3 extends the linear trend line to the x-axis to
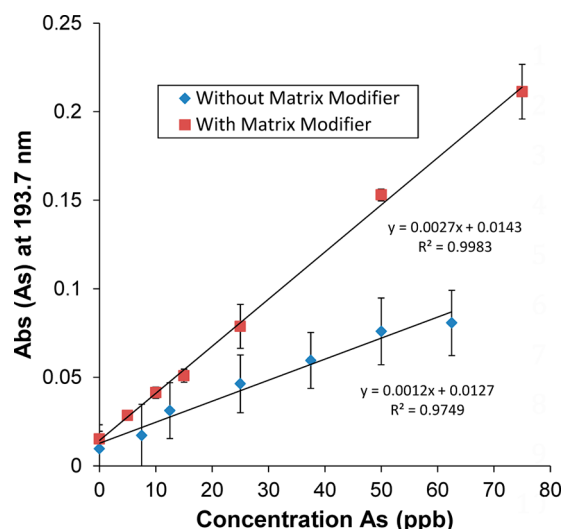

Figure 2. Arsenic calibration curves generated from the analysis of arsenic standard solutions with and without a stabilizing matrix modifier (50 ppm of $Ni(NO_3)_2$).[15] In some cases, error bars representing standard deviation are smaller than markers for average absorbance ($n = 3-4$).
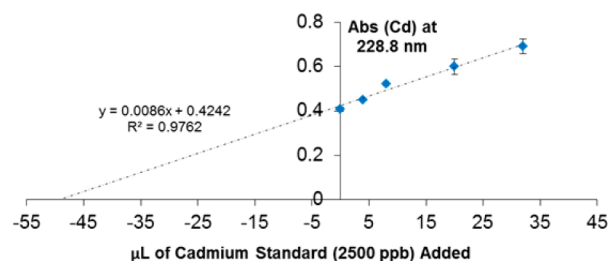

Figure 3. Standard addition plot used for the GF-AAS analysis of cadmium in a sample from black graduation beads. Successive volumetric additions of a standard cadmium solution (2500 ppb) show a linear trend in absorbance increases such that linear regression analysis translates to an x-intercept that relates to the concentration of cadmium in the original sample. In some cases, error bars representing standard deviation are smaller than markers for average absorbance ($n = 3$).

illustrate this concept. Standard addition calculations are covered in more detail in the Supporting Information. In our study, every sample determined to be noncompliant for one of the three metals was successfully confirmed using standard addition analysis.[3]

X-ray Fluorescence Analysis

While the preceding analysis of the toys is relatively inexpensive, it is also somewhat time-consuming and work-intensive. Additionally, all of the AAS analyses are destructive techniques that require destruction, digestion, and ultimately the loss of the samples. If resources allow, a contrasting nondestructive and high throughput assessment of metal content in toys/toy jewelry can be achieved via X-ray fluorescence spectroscopy (XFS), an instrument commercially available for purchase or rental for this type of project. This hand-held device directly reports metal concentrations of these and many other metals. It is useful as a confirmation technique secondary to AAS (multi-instrument) or can be used to conduct an independent study. Table 1 lists an example

comparison of toys/toy jewelry samples that were tested by both AAS and XFS during our study.

CONCLUSIONS

In addition to the studies presented, the bioavailability of the metal, the amount of metal released when a child digests or mouths a product identified as being noncompliant, may be of interest to investigate. More details for procedures[19] for such studies are included in the Supporting Information. The spectroscopic analysis of children's toys/toy jewelry illustrates numerous major aspects of quantitative and instrumental analysis including calibration curve analysis, standard addition analysis, and the use of matrix modifiers. The experiments allow for students to directly assess atomization efficiency of different atomic spectroscopy and its effect on analysis as well as the differences between destructive (e.g., GF-AAS; FL-AAS) and nondestructive (e.g., XFS) instrumental analyses. Students should be encouraged to publish interesting findings[3] or present their work and results at on-campus or local symposia as the topic usually generates significant interest from both scientific and nonscientific communities. If results on specific products from named stores are to be publicly disseminated, we advise principal investigators or instructors to first check with university legal counsel. At minimum instructors are encouraged to form a "poster session" of the project at the department level. This project module offers opportunities for student-derived, public health related hypotheses to be made making it of high interest and engagement to premedical as well as graduate bound science students.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Laboratory documentation, instructor notes and resources, student instructions, example student data and results, annotated student spreadsheet (Excel). This material is available via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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