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

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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 non-destructive 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

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1 ■ INTRODUCTION

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

9 Children under the age of six are in a critical developmental stage both physically
10 and cognitively. Due to the persistent mouthing behavior of children in this age group,
11 there is significant risk for heavy metal exposure from contaminated consumer products
12 such as children's toys.² Continual exposure to heavy metal toxins through ingestion
13 during mouthing can have serious health effects because of the accumulation of metal in
14 the body. The combination of toxic metals in certain children's toys/toy jewelry, along
15 with the accessibility of these toys to children, and children's developmental vulnerability
16 has been identified as a "risk triangle" by the Intergovernmental Forum on Chemical
17 Safety, and highlights a significant public health issue.³

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

27 The United States, along with many other countries, have enacted regulations to
28 prohibit excess amount of heavy metals in consumer products, including children's toys
29 and toy jewelry items. In 2009, the United States Consumer Product Safety Commission
30 (CPSC) created its first legal statute for the contamination of children's products with
31 lead at 300 mg/kg.⁴ Regulatory metal limits continued to be scrutinized in following

1 years as the European Union and International Standards Organization became more
2 stringent on the existence of heavy metals in children's products. In 2012, the CPSC
3 adopted the American Standards for Testing and Materials (ASTM) standard for toy
4 safety, F963-11.⁴⁵ This regulation put the United States' regulations on toy safety
5 regarding heavy metal contamination on par with those of other leading nations,
6 including the European Union (EN71 Part 3), Canada (SOR/011-17), and Australia
7 (AS/NZ ISO 8124 Part 3). The current CPSC regulation limits for this country are set at
8 25 mg/kg As, 75 mg/kg Cd, and 90 mg/kg Pb.⁶

9 Several quantitative analysis studies have specifically addressed the heavy metal
10 contamination of children's toys/toy jewelry.^{3,7,9} Weidenhamer and coworkers, for
11 example, used atomic absorption spectroscopy (AAS) and x-ray fluorescence
12 spectroscopy (XFS) to examine the lead or cadmium content in low cost metallic and
13 plastic jewelry, finding many products in excess of legal limits, as well as having jewelry
14 items with average lead levels between 30-44% of the items' weight.^{8,9} More recently,
15 Zagury⁷ and Leopold⁹ researchers performed more expansive testing of a wider range and
16 composition of children's toys/toy jewelry, including screening for arsenic, lead and
17 cadmium. While both of the latter studies addressed aspects of bioaccessibility, the
18 primary focus of Zagury et al. was a wide range of potential toxins in numerous products⁷
19 while Leopold et al. specifically examined the effectiveness of multi-technique analysis
20 and the socioeconomic implications and factors within the findings.³ Taken collectively,
21 these studies solidified an overall consensus that numerous toy products are non-
22 compliant, exceeding regulatory levels of these metals.

23 Our recent study involving multi-metal analysis of children's toys/toy jewelry
24 using multiple analytical techniques and instruments illustrates a unique and relevant
25 laboratory project that is rich in both quantitative science and public health education.³
26 Other educationally-based studies have employed atomic absorption spectroscopy for
27 lead and cadmium analysis, including Brouwer's experiment for analyzing PVC in toys
28 for the metals¹⁰ and Weidenhamer's analysis of lead in circuit boards for non-science
29 majors.¹¹ Few of the other studies we have encountered of this nature, however,
30 encompasses such a breadth of important quantitative analytical chemistry concepts while
31 also addressing a serious public health issue that relates to a range of students that include

1 those pursuing a career in the sciences (B.S., M.S., Ph.D.) as well as pre-medical (M.D.)
2 and public health (M.P.H) oriented students.

3 In the last year alone, 48,014 applicants completed on average 14 applications to
4 medical schools across the country. Of the applicants, a disproportionate number of them
5 (~65%) of them are applying to medical schools as science, technology, engineering and
6 math (STEM) majors with a significant number (4966 or ~16%) of that group applying
7 from physical sciences, including chemistry and physics.¹² Additionally, it is estimated
8 that there are over three hundred institutions that offer a graduate degree in public health
9 also drawing from STEM disciplines.¹³ In the upcoming decade, employment
10 opportunities in various public health and medical fields are projected to grow
11 significantly here in the United States in response to implementation of the Affordable
12 Care Act as well internationally with emerging global health issues.¹⁴ Within the field of
13 chemistry, pre-medical or pre-public health chemistry majors may not find the more
14 classical training in quantitative chemical analysis relevant to their perceived career
15 paths. A quantitative analysis project that analyzes children's toys for toxic metals
16 exposes these students to a very real interface of science and public health – a project that
17 allows them significant ownership of an idea because there is freedom to examine a
18 number of different toy aspects (e.g., composition, cost, origin of purchase) as well as a
19 variety of public health implications (e.g., healthcare, socioeconomic factors,
20 store/distributor location) while still encompassing a large number of basic analytical
21 skills and more advanced analysis. Within this project the conceptual and practical
22 lessons range from basic techniques of sample digestion, ppm vs. ppb concentrations,
23 dilution procedures, and pipetting as well as traditional methodology of sample analysis
24 using calibration curves and standard addition. More advanced analytical concepts are
25 also accessible within the project, including the difference between spectroscopic
26 instrumentation, most notably atomization efficiency between flame (FL) and graphite
27 furnace (GF) AAS with or without chemical additives.

28 29 ■ DESIGN/IMPLEMENTATION OF QUANTITATIVE ANALYSIS MODULE

30 The educational goals of this project module include independent student learning
31 and practice of a number of fundamental quantitative/instrumental analysis techniques

1 and concepts in the context of an interesting, public health-related research experience.
2 The numerous aspects of testing toys/toy jewelry (e.g., composition, price, location,
3 product lots, etc.) allow for students to form their own hypotheses or questions – an
4 important aspect of an effective project experience. For this paper, two undergraduate
5 (sophomore and junior) biochemistry majors enrolled in an independent study to perform
6 quantitative analysis of lead, cadmium, and arsenic in children's toys and toy jewelry
7 from bargain stores using atomic and fluorescence spectroscopies. Both students were
8 initially trained by the instructor in quantitative chemical analysis techniques, equipment,
9 and instrumentation (see below for more detail). Neither student had significant, prior
10 quantitative analysis training nor does the biochemistry major require students to take
11 quantitative analysis. After initial training, the students were charged with hypothesis
12 development, sample selection, record keeping, and digestion/analysis of samples. The
13 students ultimately devised the hypothesis of comparing a large number of inexpensive
14 toys from bargain/discount stores to similar toys purchased at major retail chains (results
15 are published elsewhere³). During the course of the semester, the students worked once a
16 week for 4 hours over 3-4 weeks, each 3-4 week segment starting from new sample
17 digestions and culminating in spectroscopic measurement of metal content in the
18 products. As will be described, the repetition of the digestion to analysis cycle is
19 conducive to student's schedules and is essentially required because calibration curves
20 have to be regenerated on a regular basis to accommodate for changes in the
21 instrumentation. The process was continually repeated and the procedures honed over
22 two semesters and two summers until 100 toys/toy jewelry items had been tested³ and the
23 detailed procedures for the 3-4 week implementation had been fully developed.

24 Depending on the specific institution's available resources, the project module
25 can be implemented in a number of ways: as part of a course, as an independent project,
26 within the scope of undergraduate research, or within a special topics course on
27 quantitative analysis or public health science. After initial training in quantitative
28 analysis techniques/equipment/instrumentation, the module described herein requires
29 approximately 3 four hour laboratory periods to generate significant results that illustrate
30 a meaningful, hypothesis-driven comparison, particularly if an entire class performs the
31 module as a group. Our suggestion is that the module be executed as part of an

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

16
17

18 ■ EXPERIMENTS

19 **Sample Selection**

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

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

5

6 **Nitric Acid Digestion and Analysis**

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

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

1 diluted sample using GF-AAS, and work towards smaller dilutions (1:10 or 1:2) if a
2 signal is not observed.

3

4 **Calibration Curve Analysis of Samples (Beer-Lambert Law)**

5 Prior to analyzing the sample solutions with AAS, calibration curves need to be
6 constructed for each metal on both FL-AAS and GF-AAS. Standardized metal solutions
7 of increasing concentrations are created based on the expected linear range of each
8 analyte, information that can usually be found in many of the handbooks, manuals, and
9 websites associated with the common AAS vendors (e.g., Varian, Perkin-Elmer). For
10 FL-AAS, the expected linear ranges for lead and cadmium are zero (i.e., blank) to 12
11 ppm and zero to 5 ppm, respectively. According to standard methods,¹⁵ arsenic requires a
12 higher level of atomization and was not tested using FL-AAS (see Table 1 below). These
13 standardized solutions are created in volumetric flasks from 1000 ppm stock metal
14 solutions and diluted with ultra-pure water (see Instructor's Notes, Supporting
15 Information for example preparation). Multiple replicates of each standard should be
16 made to encompass measurement and instrument variability. Blank measurements as
17 well as known standard samples in nitric acid should be routinely checked against the
18 working calibration curve as a quality control to indicate if a new calibration curve
19 should be generated, an especially important aspect of experiments that are ongoing over
20 the course of weeks. An example of a calibration curve and linear regression analysis
21 for lead using FL-AAS is shown in **Figure 1A**. Sample calibration curve data for both
22 the flame and furnace AAS for lead, cadmium, and arsenic are provided as part of the
23 Supporting Information. After establishing acceptable calibration curves and subsequent
24 best-fit-linear regression analysis performed, the absorbance of the sample digest should
25 be measured to determine the ppm concentration of the metal in the sample digest
26 solution.

27 If the samples do not contain ppm metal concentrations a similar procedure is
28 used to prepare a calibration curve for GF-AAS analysis, a technique with ppb detection
29 capability. Standards for the furnace should be created in a similar manner to those
30 above. The concentration ranges will be much lower, however, and may require a new
31 stock solution to be made. Standard concentration ranges for As, Cd, and Pb are 0-75

1 ppb, 0-40 ppb, and 0-400 ppb, respectively. It should also be noted that the furnace
 2 requires a much smaller volume of sample during analysis, allowing standards to be made
 3 in 25 mL volumetric flasks. Arsenic analysis using GF-AAS is aided greatly with the
 4 addition of $\text{Ni}(\text{NO}_3)_2$, a chemical additive, matrix modifier that was added to all arsenic
 5 standards and samples.¹⁵

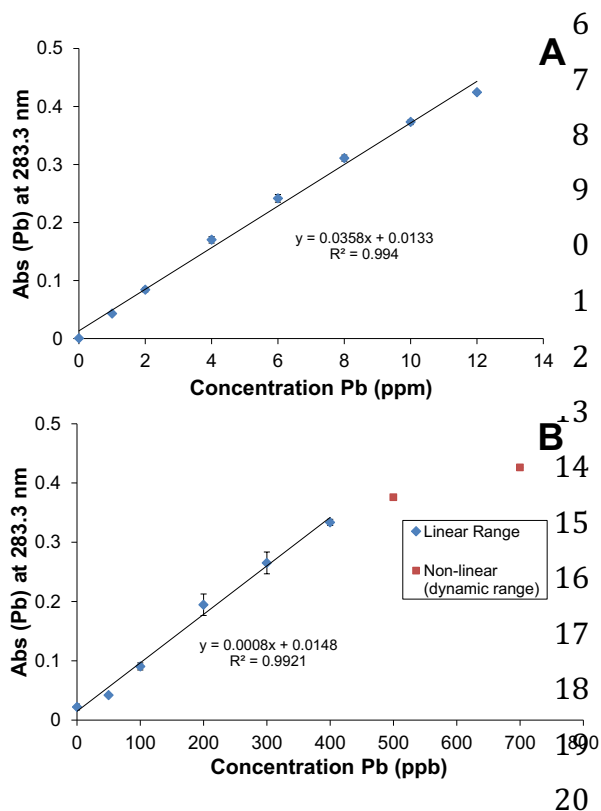


Figure 1. Lead calibrations curve generated from the analysis of lead standard solutions using (A) FL-AAS and (B) GF-AAS. Linear regression analysis for the “best fit straight line” in both graphs used to determine the concentration of lead in toy and toy jewelry sample digests. Note: In some cases,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

21 Standard Addition Analysis (Matrix Compensation)

22 Because many of the children’s toy/toy jewelry samples have complex matrices,
 23 standard addition analysis provides an effective method for more accurate metal
 24 concentration determination. Standard addition analysis using GF-AAS is conducted on
 25 the samples identified as contaminated (non-compliant) through calibration curve
 26 analysis. For each of these samples, 4-5 solutions are created from the sample’s original
 27 digestion solution in 2 mL volumetric flasks with successive additions of standard metal
 28 solution. Standard solutions are added to these flasks so that the absorbance of the final
 29 solution is 1.5 to 3 times that of the original sample digest (i.e., no standard added).¹⁶ All
 30 of the flasks are diluted to volume. While the volume of added stock solution (of known

1 concentration) will increase incrementally, the final volume (2 mL) remains constant.
2 These solutions should then be analyzed using GF-AAS.

3

4 **X-Ray Fluorescence Spectroscopy Analysis**

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

9

10 **Data Analysis**

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

17

18 **Hazards**

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

25

26 **■ RESULTS AND DISCUSSION**

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

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2

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4 **Calibration Curve Analysis**

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

20

21 **Calibration Curve Analysis Using Matrix Modifiers**

22 The analysis of arsenic using GF-AAS allows students to consider the benefit of
23 matrix modifiers, the most common examples covered in quantitative analysis courses
24 being releasing agents and ionization suppressors to combat chemical and ionization
25 interferences, respectively.^{16,18} Because of arsenic's volatility, the analysis of arsenic
26 requires a stabilizing or protective agent ($\text{Ni}(\text{NO}_3)_2$) to be used to form stable but volatile
27 complexes with arsenic. Complexation with $\text{Ni}(\text{NO}_3)_2$ allows for increased atomization
28 efficiency and, ultimately, the sensitivity of the technique by extending the resident time
29 of the analyte within the source light traversing the graphite furnace tube.¹⁵ GF-AAS
30 analysis for arsenic in our samples was preceded with creating standards and samples
31 containing 50 ppm $\text{Ni}(\text{NO}_3)_2$. Addition of the matrix modifier has a significant effect on

1 the calibration curves as shown in **Figure 2**, including higher sensitivity, greater linearity,
 2 and lower measurement variability.

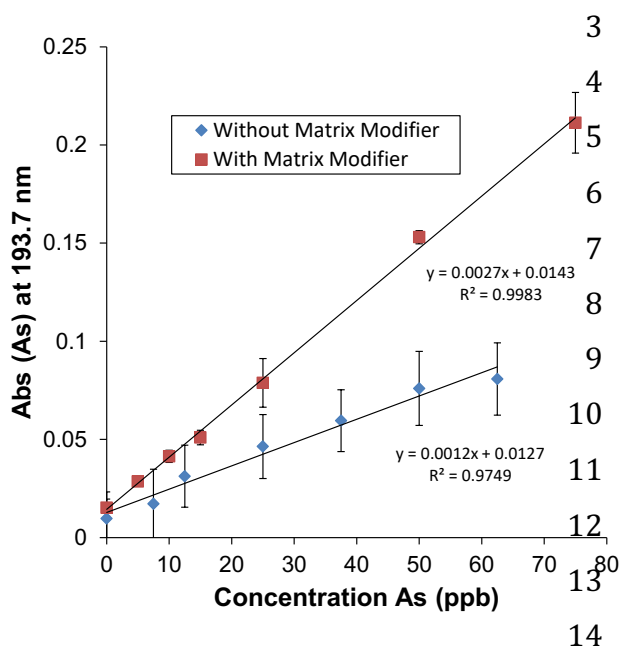


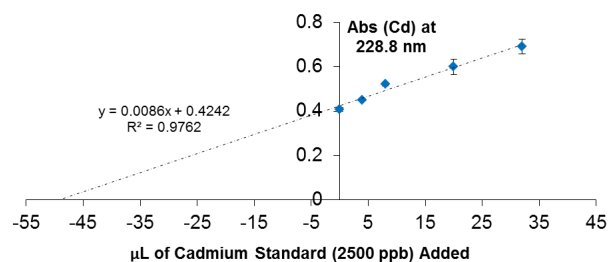
Figure 2. Arsenic calibration curves generated from the analysis of arsenic standard solutions with and without a stabilizing matrix modifier (50 ppm $\text{Ni}(\text{NO}_3)_2$).¹⁵ Note: In some cases, error bars representing standard deviation are smaller than markers for average absorbance (n=3-4).

15

16 Standard Addition Analysis

17 The matrix complexity of some of the toy/toy jewelry digests make these samples
 18 excellent candidates for standard addition analysis, a superior matrix matching
 19 technique.^{16,18} In this case, standard addition analysis was used to confirm the non-
 20 compliant levels of a metal with the assumption that matrix matched samples. Starting
 21 with the sample digest, standard solution spikes were added to the sample to create
 22 constant volume standard addition plots such as the one provided in **Figure 3**. Linear
 23 regression analysis of the data reports an equation of a straight line whose x intercept is
 24 then used to calculate the metal concentration in the original solution (i.e., the sample
 25 digest without any added standard). The plot shown in Figure 3 extends the linear trend
 26 line to the x-axis to illustrate this concept. Standard addition calculations are covered in
 27 more detail in the Supporting Information. In our study, every sample determined to be
 28 non-compliant for one of the three metals was successfully confirmed using standard
 29 addition analysis.³

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6 **X-ray Fluorescence Analysis**

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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 that linear regression analysis translates to an x-intercept that relates to the concentration of cadmium in the original sample. Note: In some cases, error bars representing standard deviation are smaller than markers for average absorbance (n=3).

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 non-destructive and high through-put 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 handheld device directly reports metal concentrations of these and many other metals. It is useful as a confirmation secondary technique 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.

1 **Table 1.** Selected Averages of Metal Concentrations From a Multi-Technique/Multi-Instrument
 2 Analysis of Lead, Cadmium, and Arsenic in Children's Toys and Toy Jewelry.

Sample Description	Metal	CPSC Regulatory Limit (ppm)	Calibration Curve FL-AAS (ppm)	Calibration Curve GF-AAS (ppm)	Standard Addition GF-AAS (ppm)	XFS Analysis (ppm)
Black Celebration Beads	Pb 283.3 nm	90	3288 (±3983, n=4)	2442 (±1196, n=2)	2881 (±50, n=2)	3346 (±2459, n=3)
Colorful Metal Rings	Pb 283.3 nm	90	ND n=2	41 (±41, n=3)	227 n=1	130 (±112.4 n=3)
Gold Chain Charm Necklace	Cd 228.8 nm	75	13 (±18, n=2)	71 (±99, n=2)	2182 n=1	2317 (±2416, n=3)
Gold Chain Charm Necklace	As 193.7 nm	25	N/A	95 (±74, n=3)	106.3 n=1	3372 (±970, n=3)

3 **Notes:** CPSC = Consumer Product Safety Commission regulatory limit; ND = non-determinable; n = number of
 4 replicates; Uncertainty is standard error.

5
 6 -Significant variability for sample measurements by individual techniques is common in this type of study and is likely
 7 related to differences in manufacturing lots of the products and opportunistic use of raw materials by foreign
 8 manufacturers.³⁷ In addition, variations between the different instrumental analyses and techniques is likely due to their
 9 inherent differences such as atomization efficiency (FL-AAS vs. GF-AAS), or matrix effects (calibration curve vs.
 10 standard addition), for examples.

11 ■ CONCLUSIONS

12 In addition to the studies presented, the bioavailability of the metal, the amount of
 13 metal released when a child digests or mouths a product identified as being non-
 14 compliant, may be of interest to investigate. More details for procedures¹⁹ for such studies
 15 are included in the Supporting Information. The spectroscopic analysis of children's
 16 toys/ toy jewelry illustrates numerous major aspects of quantitative and instrumental
 17 analysis including calibration curve analysis, standard addition analysis, and the use of
 18 matrix modifiers. The experiments allow for students to directly assess atomization
 19 efficiency of different atomic spectroscopy and its effect on analysis as well as the
 20 differences between destructive (e.g., GF-AAS; FL-AAS) and non-destructive (e.g.,
 21 XFS) instrumental analyses. Students should be encouraged to publish interesting
 22 findings³ or present their work and results at on-campus or local symposia as the topic
 23

1 usually generates significant interest from both scientific and non-scientific communities.
2 If results on specific products from named stores are to be publically disseminated, we
3 advise principal investigators or instructors to first check with university legal counsel.
4 At minimum instructors are encouraged to form a “poster session” of the project at the
5 department level. This project module offers opportunities for student-derived, public
6 health-related hypotheses to be made; making it of high interest and engagement to pre-
7 medical as well as graduate bound science students.

8

9

10 ■ ASSOCIATED CONTENT

11 Supporting Information

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

15

16 ■ AUTHOR INFORMATION

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20

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1

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