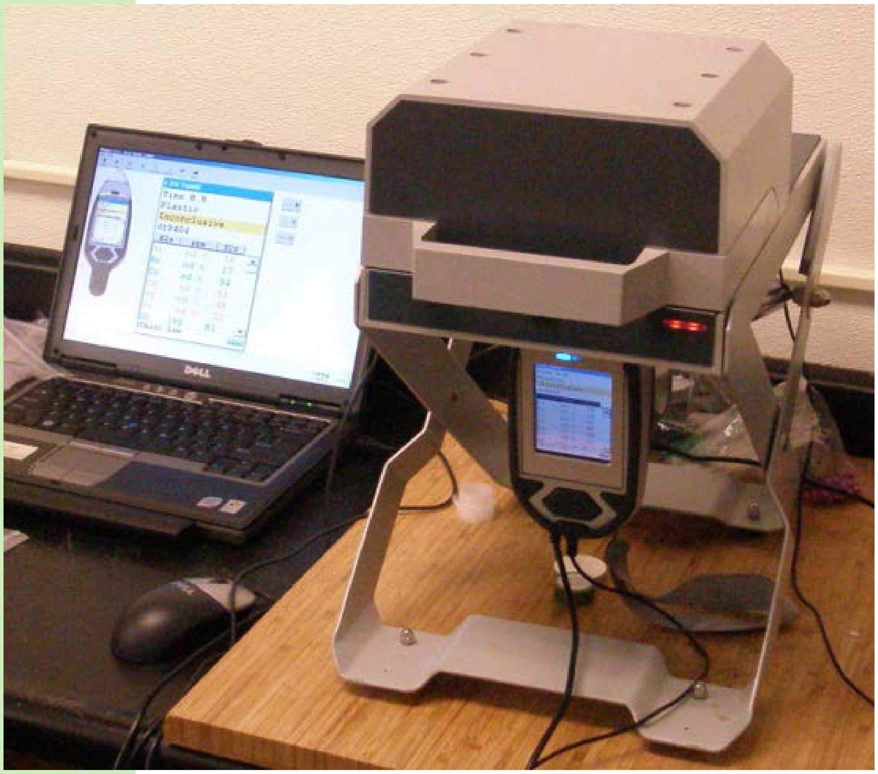

Evaluation of XRF as a Screening Tool for Metals and PBDEs in Children's Products and Consumer Goods

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Cover photo: Niton XRF Analyzer and Stand.

Evaluation of XRF as a Screening Tool for Metals and PBDEs in Children's Products and Consumer Goods

by

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Abstract

In 2011, the Department of Ecology conducted a study to compare handheld x-ray fluorescence (XRF) and laboratory measurements of contaminant levels in children's products and consumer goods to assess the usefulness of XRF technology as a screening tool. XRF screenings were conducted on individual components from over 300 children's products and consumer goods for a suite of analytes: antimony, arsenic, bromine, cadmium, cobalt, lead, mercury, and molybdenum.

Seventy-two samples were forwarded to the laboratory for analysis of all above analytes except bromine, using traditional techniques. Fifty-seven of those samples were digested using a total decomposition method and were used in the comparison to XRF data. In addition, 68 samples were measured for 6 PBDE congeners (BDE-47, -99, -100, -153, -154, and -209) to compare with XRF-measured bromine results.

Overall, handheld XRF readings provided adequate results for metal analytes if care was taken in sample pre-processing. The XRF analyzer produced a large number of false positives for the metal analytes when products were measured on non-isolated components by hand. Very few false negatives occurred in the analysis. XRF readings on isolated components of products compared well with laboratory results, with r^2 typically > 0.90. If XRF is used to screen intact products, samples should be isolated and measured in a stand to confirm the original analysis.

The majority of samples with XRF-measured bromine did not contain PBDEs above detection limits. When both XRF-measured bromine and PBDEs were present, poor relationships ($r^2 < 0.50$) and high sample-specific relative percent differences were found. PBDEs represented a very small fraction of the total bromine present. There were no cases where PBDEs were detected in absence of XRF-measured bromine, indicating that XRF may be useful as a screening tool to identify samples that *could* contain PBDEs.

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Introduction

In 2008, the Children's Safe Product Act (CSPA) was signed into Washington State law (Children's Safe Product Act, 70.240 RCW) to reduce children's exposure to toxic chemicals. A portion of the law required the Department of Ecology (Ecology), in consultation with the Department of Health, to create a list of chemicals that, when present in children's products, manufacturers must report. In response, the CSPA Reporting Rule was recently created and identifies 66 chemicals and classes of chemicals of high concern (Chapter 173-334 WAC). Reporting requirements will begin with the largest manufacturers who make products intended for mouth or skin contact. Other manufacturers will begin reporting in a phased-in schedule included in the rule.

In 2007, the legislature passed Washington State's Polybrominated Diphenyl Ether (PBDE) law (PBDE Rule, Chapter 70.76 RCW) in part due to the findings of the PBDE chemical action plan (Peele, 2006). The final portion of the PBDE law became effective in January of 2011, placing restrictions on all three primary PBDE formulations. Penta-BDE and octa-BDE formulations were banned completely; deca-BDE was banned in mattresses, televisions, computers, and residential upholstered furniture. For practical purposes, the "ban" limited concentrations of PBDEs to less than 1000 ppm (0.1%) (Ecology, 2008).

In order to reduce the cost associated with enforcement of both laws, Ecology is exploring the use of a portable x-ray fluorescence (XRF) spectrometer to pre-screen samples for laboratory analysis. The ease of use, time, and cost savings of XRFs for measuring inorganic elements has made the instruments increasingly popular. The purpose of the present study is to determine the efficacy of XRF for screening of selected metals and PBDEs in consumer goods.

XRF Background

XRF works by dislodging lower energy level electrons with an x-ray beam. The vacated lower energy orbitals are replaced by electrons from higher energy orbitals, releasing a characteristic energy of the type of atom present. XRF interprets the energy signal to calculate elemental concentrations (Thermo Fisher Scientific, 2009). Figure 1 displays the Niton XL3t handheld XRF analyzer used in the study.

The use of XRF methods for determining metals in media such as soils and metal alloys has been well established. With recent regulations in the U.S. and European Union restricting certain elements in consumer products, there has been increasing interest in using XRF as a non-destructive screening tool for matrices such as plastics, textiles, and metals. Several studies have examined the comparability of XRF analyses with traditional laboratory measurements in consumer product samples (e.g. Cobb, 2009; USACE, 2008; TPCH, 2011; Allen et al., 2008).

The development of methods and guidance concerning the use of XRF for analysis of metals in consumer products is also growing. ASTM International published a standard test method for the identification and quantification of several metals in homogenous polymeric material using energy dispersive X-ray spectrometry in 2008 (ASTM F 2617-08). A Standard Operating Procedure of the U.S. Consumer Product Safety Commission allows the use of XRF for determining lead in polymeric materials, with certain limitations (CPSC-CH-E1002-08). Guidance from the European Union allows for screening of regulated elements in consumer products by XRF (REGD V.1, 2006).

This study evaluates the performance of an XRF analyzer for a variety of elements included in the CSPA reporting rule (antimony, arsenic, cadmium, cobalt, molybdenum, and mercury) and lead by comparing them to laboratory measurements. The relationship between XRF-measured bromine and laboratory-measured PBDEs is also examined.

Figure 1. Niton XL3t Handheld XRF.

Study Goals and Objectives

In response to the CSPA Reporting Rule and PBDE ban, the Environmental Assessment Program conducted a study measuring 6 potentially toxic metals required to be reported under the CSPA reporting rule (antimony, arsenic, cadmium, cobalt, molybdenum, and mercury), lead, and 6 PBDE congeners (BDE-47, 99, 100, 153, 154, 209) in children's products. The primary goal of the study is to assess the usefulness of XRF methods as a screening tool for the metals of interest and for bromine to indicate the possibility of PBDE presence in children's products and consumer goods.

Specific objectives were to:

1. Take an initial screening of individual components from approximately 300 products with the handheld XRF analyzer. Components are not isolated from the original product during this screening; multiple measurements are made on the same product without disassembly.

2. Measure approximately 70 isolated product components under a variety of XRF operating conditions for the metals of interest in the CSPA rule. Analyze the same samples for CSPA metals using traditional laboratory techniques.

3. Measure approximately 70 isolated product components under a variety of XRF operating conditions for bromine. Analyze the same samples for PBDEs using traditional laboratory techniques.

4. Compare results of XRF and laboratory measurements of metal analytes to assess XRF precision and accuracy.

5. Determine if XRF can be used to evaluate the possibility of PBDE presence in consumer products by testing for bromine.

6. Make recommendations concerning the use of XRF as a screening tool.

Study Design

Products were collected from 7 Puget Sound area retailers, an internet retailer, and an electronics recycling facility. Figure 2 displays a categorical breakdown of the items selected. Detailed information on product selection, product screening, and target chemicals is provided in the Quality Assurance (QA) Project Plan for this study (Furl, 2011).

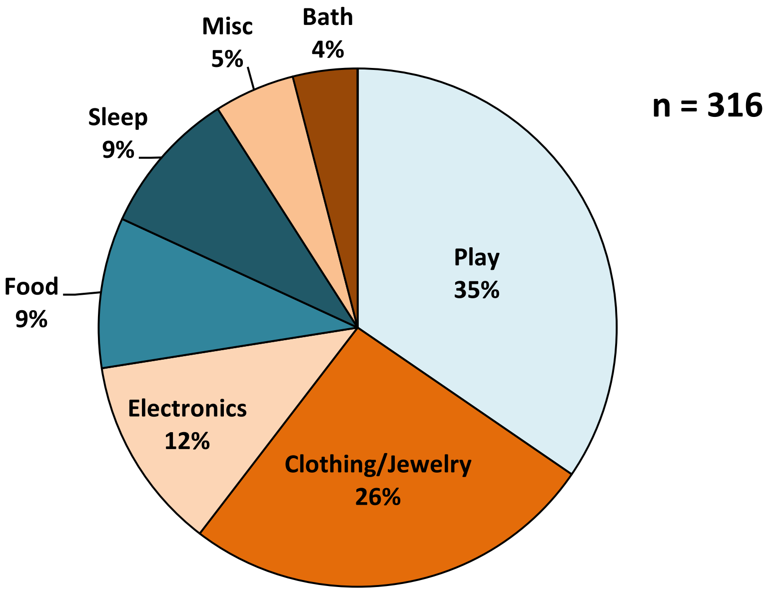

Figure 2. Categorical Descriptions of Items Collected for XRF Testing.

Items were screened using a Niton XL3t handheld XRF spectrometer rented from the manufacturer. Based on the screening results, a subset of samples covering a wide range of concentrations was chosen for laboratory analysis. XRF measurements were repeated on samples chosen for laboratory analysis under a variety of sample processing methods and XRF operating conditions.

Laboratory analytes for metals included antimony, arsenic, cadmium, cobalt, lead, mercury, and molybdenum. PBDE samples were measured for BDE-47, -99, -100, -153, -154, and -209.

Methods

Sample Collection

In total, 316 new products were collected. A wide variety of product types were included, mostly focusing on those targeted for children between the ages of 0-5 years. Products were selected based on targeted use population (for example toddlers or infants) and type of use, such as play toy, apparel, food ware, or bedding. Selections included a variety of material types and colors.

Additionally, 36 electronics housings salvaged from a local recycling facility were collected in order to provide samples likely to contain PBDEs. Product manufacturing dates, when available, were considered in the selection of these components in order to find components manufactured prior to the PBDE ban. Recycled electronics were also collected to ensure data would exist with which to compare PBDE results and XRF measurements of bromine. It was anticipated very few new products would contain PBDEs due to legislation banning their sale and due to voluntary product withdrawal by industry.

Collected samples were brought back to Ecology headquarters where they were removed from their packaging and assigned a unique alphanumeric number. A photograph of each item was taken and product details were collected such as country of manufacture, manufacturer, distributer, Universal Product Code, SKU code, intended age for toy, and matrix type. Samples were stored in a secure chain of custody room until forwarded to the laboratory.

XRF Analyses and Sample Preprocessing

XRF Measurements

XRF measurements were conducted four different ways to examine the effect of sample processing and XRF settings. First, an initial screening was conducted, followed by material isolation screenings by hand and in-stand, and lastly cryomilled materials were measured. *By hand* refers to measurements made while holding the XRF analyzer in hand and manually pulling a trigger. Measurements can also be made *in-stand* where the analyzer is docked in a stationary stand and remotely activated. *Cryomilling* refers to the process of reducing a sample to very small particle sizes by employing cryogenic temperatures and a mechanical mill. Further details on each of the measurements are included below. All samples were measured in Niton's TestAll® mode.

Initial Screening

All components of each individual item underwent an initial 30-second handheld XRF screening. Components were defined as items with different colors or base materials including materials not meant to be handled, e.g., stuffing from pillows or comforters. During the initial screening, subcomponents were measured while still attached to the original product, i.e., not isolated. Data collected were merged with the spreadsheet constructed during sample cataloguing, using the unique alphanumeric number.

During the initial screening effort, 30 items were randomly selected for duplicate analyses. Duplicates were performed for approximately the same amount of time as the original analysis. Here and throughout the project, duplicate (and triplicate) analyses were performed by taking an additional reading immediately after the original analysis without moving the analyzer.

Sample Selection

Seventy-two sample components were selected for further XRF screening and laboratory analysis of metal analytes. To determine which products to further analyze, results from the initial 30-second screening were reviewed for a range of concentrations and analytes. Items were selected for metals analysis if the XRF indicated an appreciable amount of one of the metals of interest.

A range of concentrations for each element were selected from near XRF limits of detection (LODs) to several thousand ppm. Products from both the high and low end of the concentration spectrums were included to gauge performance at both ends. Additionally, a mix representing all material types (plastics, metals, textiles), product types (play toy, apparel, bedding, food ware) and retailers were selected from the products exhibiting detections. Each sample selected was analyzed for all seven elements of interest.

Sixty-eight samples were selected for PBDE analysis, based on bromine content detected during the screening phase. In addition to high concentration samples (primarily recycled electronics), approximately 20 samples with low or no detected bromine were analyzed for PBDEs to examine the possibility of false negatives.

Material Isolation Screening

After samples were selected for screening, the specific component of interest was isolated from the product. This was done in order to remove interfering materials which may have confounded the initial XRF screening. Components were removed with clean (nitric- and acetone-rinsed) stainless steel tools including scissors, saws, and a handheld rotary tool.

The isolated material was re-examined by the XRF for 60 seconds by handheld measurements and for 60 seconds using the XRF bench-top stand. Materials were folded or stacked when necessary to provide a thickness of at least 0.5 cm.

A subset of the samples forwarded to the laboratory was measured in 30, 60, and 90 second increments to assess precision across different timeframes. These measurements were carried out during the isolated material XRF screenings both by hand and in the stand.

Cryomilling

Plastic samples were shipped to Toy Testing Inc. where they were cryomilled following established laboratory guidelines (Toy Testing Lab, 2010). Milled samples were returned to Ecology and measured by XRF in the stand (hereafter referred to as “powder” analysis).

Samples that could not be milled by the laboratory (fabrics, foams, and metals) were cut into small pieces (<1 cm) and forwarded to the laboratory. Cryomilling could not be done on foam products because small pieces of foam clump together even under extremely low temperature. Fabric pieces were also not suitable for cryomilling because the mill uses a ball bearing in the vessel to grind the sample; fabric pieces can bind together and be packed by the ball rather than pulverized. Metal materials are also not compatible with cryomilling because metal substrates would damage the cryo vessel.

Laboratory Procedures

Metals Analysis

Antimony, arsenic, cadmium, cobalt, lead, and molybdenum were analyzed at Ecology’s Manchester Environmental Laboratory (MEL) using inductively-coupled plasma mass spectrometry (ICP-MS). Mercury samples were analyzed using cold vapor atomic absorption (CVAA).

Samples were prepared using either EPA Method 3052 (using hydrochloric acid in lieu of hydrofluoric acid) or EPA method 3050B (except for mercury analyses). Method 3052 uses microwave assist and concentrated hydrochloric acid in order to completely digest the sample, while method 3050B uses a hot plate and acid for digestion and is considered a leaching test. Digestion method is an important consideration when comparing to XRF results. XRF results report a total concentration and are analogous to the 3052 method.

Fifty-seven of the samples selected for laboratory analysis consisted of non-metal materials (plastics, textiles, rubber, and foam) and were prepared using EPA method 3052 (using hydrochloric acid in lieu of hydrofluoric acid). Fifteen samples consisted of metal material and were prepared following EPA method 3050B because MEL’s policy dictates that metal materials are not compatible with their microwave hardware.

A small portion of the samples (n = 6) were digested using EPA method 3052 with hydrofluoric acid by Brooks Rand Laboratory. These samples consisted of siliceous materials (glass and silicones) where concentrated hydrochloric acid was not sufficient to completely digest the material.

Mercury samples were digested and analyzed following EPA method 245.5. With this method, microwave assist is not used and the digestion technique is more similar to 3050B than 3052.

Table 1 displays the preparation and analysis techniques.

Table 1. Laboratory Techniques for Metals Analysis.

Product matrix	Analyte	Preparation	Analysis	Laboratory
All types	Hg	EPA 245.5	EPA 245.5 - CVAA	MEL
Non-metal	As, Cd, Co, Mo, Pb, Sb	EPA* 3052	EPA 200.8 - ICP MS	MEL
Non-metal	As, Cd, Co, Mo, Pb, Sb	EPA^ 3052	EPA 200.8 - ICP MS	Brooks Rand
Metal	As, Cd, Co, Mo, Pb, Sb	EPA 3050B	EPA 200.8 - ICP MS	MEL

* With hydrochloric acid in lieu of hydrofluoric

^ With hydrofluoric acid

CVAA - cold vapor atomic absorption

ICP MS - inductively-coupled plasma mass spectrometry

See appendix A for metals abbreviations

PBDE Analysis

PBDEs (-47, 99, 100, 153, 154, and 209) were analyzed by Rhode Island Analytical (RIAL) in six separate batches. Samples were extracted by Soxhlet extraction following modifications of EPA SW-846 3540. Samples were concentrated, acid cleaned, and analyzed by gas chromatography electron capture detection (GC/ECD) using dual column confirmation. Numerous samples were also confirmed using gas chromatography mass spectrometry (GCMS) (data not shown).

Data Quality

XRF

The accuracy and precision of XRF results were evaluated through the analysis of quality assurance measures and how well they compared to laboratory results. Quality assurance measures included duplicates, triplicates, and analysis of certified standards. Results of XRF data quality measures are included in the *Results and Discussion* section.

Laboratory

MEL prepared written case narratives assessing the quality of the laboratory data collected for the project. The reviews included a description of the methods and an assessment of holding times, initial and continuing calibrations, method blanks, matrix spikes, matrix spike duplicates, laboratory control samples, and surrogate recoveries. Case narratives are available upon request. Measurement quality objective (MQO) targets outlined in the QA Project Plan are shown in Table 2 and reviewed below. Complete results of all MQOs are shown in Appendix C.

Table 2. Measurement Quality Objectives for Laboratory Analyses.

	Laboratory Control Samples (recovery)	Matrix Spikes (recovery)	Duplicates† (RPD)	Method Blanks* (ppm)	Surrogate Recovery (recovery)
Antimony	85 - 115%	75 - 125%	± 20%	4	
Arsenic	85 - 115%	75 - 125%	± 20%	2	
Cadmium	85 - 115%	75 - 125%	± 20%	2	
Cobalt	85 - 115%	75 - 125%	± 20%	2	
Lead	85 - 115%	75 - 125%	± 20%	2	
Mercury	85 - 115%	75 - 125%	± 20%	0.1	
Molybdenum	85 - 115%	75 - 125%	± 20%	2	
PBDEs	40 - 140%	40 - 140%	± 25%	1	30 - 150%

† Matrix spike duplicates and split duplicates
* Metals reporting limits were estimated by raising soil limits by a factor of 20
RPD: Relative percent difference
ppm: parts per million

Metals

Data for the metals analysis were generally within the MQO targets outlined in Table 2. Instances where MQOs were not achieved or standard laboratory procedures were outside of acceptance limits included:

- Several calibration checks (continuous and blank) were outside of acceptance limits resulting in qualifying the data as estimated.
- A single pair of antimony duplicates was outside of MQOs. The native sample was qualified as an estimate.
- Several matrix spikes for antimony, lead, and mercury were outside of MQOs.

Samples analyzed by Brooks Rand with the hydrofluoric digestion were within MQOs with the exception of a single matrix spike for cadmium. The source sample was qualified "J" as an estimate.

PBDEs

The majority of MQOs were met for PBDE analyses with several exceptions.

- Numerous surrogate recoveries were outside of the 30-150% limits set.
- LCS samples were recovered high in two of the batches.
- Matrix spike recoveries were low for sample #AZ1308 (BDE 209) and high for #DT0404 (BDE 209).

Additionally, instrument calibration procedures were outside of laboratory-identified targets in several instances. This, along with the MQO violations, resulted in many results being qualified as estimates.

Results and Discussion

XRF Results

XRF Detection Limits

Figure 3 displays the spread of XRF detection limits for plastic and metal matrices during the initial 30-second screening phase. “Plastic” matrices include all non-metal matrices such as textiles and foams. Limits of Detection (LODs) were calculated by multiplying the XRF-reported 2 sigma error by 1.5 (Thermo Fisher Scientific - personal communication). Detection limits vary greatly depending on sample matrix and testing time.

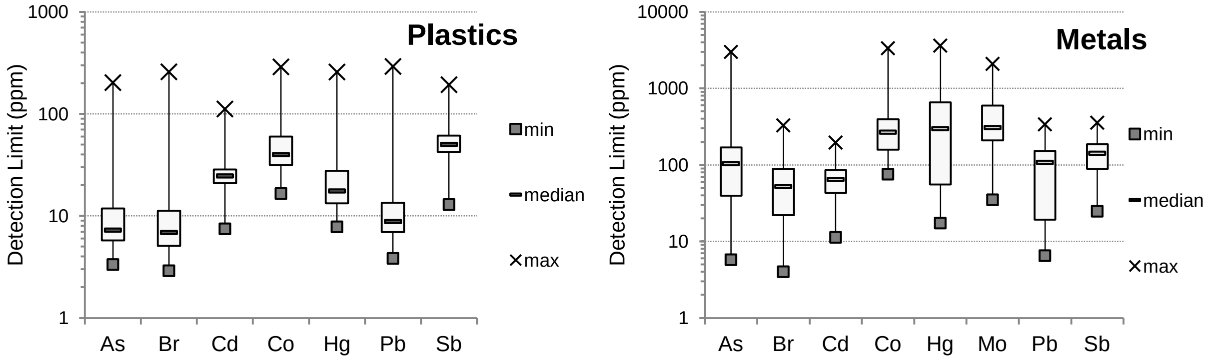

Figure 3. Range of Detection Limits for XRF Measurements.

Top and bottom lines of rectangles represent 75th and 25th percentiles, respectively.
Data include only initial 30-second screening measurements and any values > LOD were excluded.
“Plastics” includes all non-metal product matrices, including textiles and foams.
Y axis is on logarithmic scale.

Median LODs for the elements shown in Figure 3 ranged from 9-50 ppm in plastic products and from 52-307 ppm in metal matrices. Minimum LODs achieved in plastic samples were less than 10 ppm for all elements except for cobalt (17 ppm) and antimony (13 ppm). For metal samples, minimum LODs were more variable and ranged from 4-75 ppm. Minimum LODs were likely achieved in low-density matrices with minimal interference. Detection limits differed greatly between the metal and plastic matrices (note difference in logarithmic scale in Figure 3).

Median LODs in the initial screening of plastic products were within the range of the manufacturer-stated LODs for polymers, with one exception. Antimony measurements had a higher median LOD than the manufacturer’s range. Median LODs from metal products were below the manufacturer-stated LODs (based on a tin matrix), with the exception of mercury (297 ppm) and lead (307 ppm), which were higher.

Detection limits for plastic matrices were generally lower than the 100 ppm reporting threshold for contaminants in children's products established in the rule (173-334 WAC). Ninety-one percent of cobalt LODs were below 100 ppm, and 98-100% of all other element readings were below 100 ppm. Detection limits for metal products were much higher, with the exception of bromine and cadmium. Only 1% of cobalt LOD measurements were below 100 ppm, and less than 50% of arsenic, mercury, lead, antimony, and molybdenum LODs were below 100 ppm.

The detection limits described above were achieved using an XRF testing time of 30 seconds. For most matrices, increasing the analysis time will reduce the detection limits by the square root of the increased time. Additional analyses would be needed to quantify achievable detection limits at longer testing times.

XRF Screening Results

In total, 1178 components from 316 individual children's products and 36 recycled electronics samples were screened using handheld XRF. Summary statistics for results that were greater than the XRF limit of detection (LOD) are provided below in Table 3.

Table 3. Statistical Summary of > LOD XRF Results for Initial 30-second Screening (n = 1178).

	Arsenic (ppm)	Bromine (ppm)	Cadmium (ppm)	Cobalt (ppm)	Mercury (ppm)	Molybdenum (ppm)	Lead (ppm)	Antimony (ppm)
% > LOD	7.9%	40.7%	6.1%	6.0%	3.1%	0.3%	12.1%	32.5%
Minimum	4.70	2.43	7.05	21.0	51.0	274	6.06	14.7
25th Percentile	25.6	8.02	14.3	54.6	278	1140	32.0	70.4
Median	96.8	16.6	56.4	183	760	1450	82.5	130
Mean	300	3800	428	2450	1010	1270	2230	1600
75th Percentile	283	62.8	122	3020	1280	1580	266	171
Maximum	5250	127000	6150	24900	6880	1890	203000	43000

Bromine and antimony were the most frequently detected elements. Detections for the remaining elements were infrequent. Lead was the only other element detected at a rate greater than 10%. Due to XRF limitations, molybdenum results were limited to products constructed of metal material. The XRF analyzer uses molybdenum as the main filter material when analyzing plastics, which excludes low level detections of molybdenum in a non-metal sample.

In children's products, jewelry samples contained the highest median concentrations of arsenic, cadmium, and lead. The highest levels of bromine and cobalt were measured in kid's furniture products. Foams from chairs and couches were high in bromine and several metal furniture frames tested high in cobalt. Antimony was detected the most frequently and at the highest levels in clothing, which included sleepwear and bedding such as sleeping bags. Bromine was detected most frequently in clothing, followed by furniture and toys. Products were not randomly selected and therefore should not be considered a representative sampling of products on the market. Summary statistics of initial screening measurements by product type are included in Appendix D.

XRF Data Quality

Duplicates/Triplicates

Precision of the XRF data were examined through analysis of duplicate measures. Samples were also screened in triplicate to assess precision of screening methods as a function of time. Duplicate and triplicate measurements were taken in succession, without moving the sample between screenings.

Initial screening duplicates

Measurements were duplicated for six metal products and twenty-four plastic products during the initial screening process. Duplicates were run for approximately the same amount of time by hand. Relative percent differences (RPDs) for duplicates are shown in Tables 4 and 5.

Table 4. Relative Percent Differences in Duplicate Screenings of Plastic Products.

Element	n	# < LOD	# NC	# > LOD	mean RPD
Arsenic	24	21	1	2	24.4%
Bromine	24	13	1	10	10.2%
Cadmium	24	24	0	0	---
Cobalt	24	24	0	0	---
Mercury	24	23	0	1	39.3%
Lead	24	22	1	1	20.1%
Antimony	24	13	1	10	13.4%

LOD: limit of detection (< LOD indicates both samples were below detection limits).
NC: not calculated because one of the two samples was below detection limits and one was quantified.

Table 5. Relative Percent Differences in Duplicate Screenings of Metal Products.

Element	n	# < LOD	# NC	# > LOD	mean RPD
Arsenic	6	5	0	1	2.1%
Bromine	6	3	1	2	6.7%
Cadmium	6	3	0	3	11.0%
Cobalt	6	6	0	0	---
Mercury	6	5	1	0	---
Lead	6	2	1	3	2.5%
Antimony	6	2	1	3	8.2%
Molybdenum	6	5	0	0	---

LOD: limit of detection (< LOD indicates both samples were below detection limits).
NC: not calculated because one of the two samples was below detection limits and one was quantified.

Only four elements were above the LOD in at least one set of duplicate samples on metal products: arsenic, cadmium, lead, and antimony. Mean RPDs for these elements were low, indicating good precision.

Analytes in plastics were also infrequently detected in the duplicates, except for antimony, which was quantified in almost half of the duplicate samples. Duplicate RPDs for arsenic, lead, and antimony were higher for plastics than metal products although they remained less than 25%. Mercury was detected in only one pair of measurements and results indicated poor precision (39% RPD) in that pair.

Triplicates

Relative standard deviations (RSDs) in triplicate measurements consisting of 30-, 60-, and 90-second intervals are shown in Tables 6 and 7. The triplicate analyses were performed on isolated components using the handheld method and in the stand to assess variability in XRF screenings due to measurement time.

Similar to the duplicate results, triplicate analyses using different time intervals produced an RSD typically < 25%. Little difference existed between RSDs for the stand and handheld methods. The low RSDs indicate that the XRF analyzer produced similar results regardless of testing time.

Table 6. Relative Standard Deviations (RSDs) in Triplicate Screenings of Metal Products.

Metals Triplicate Samples - Handheld						Metals Triplicate Samples - Stand					
Analyte	n	# < LOD	# NC	# > LOD	mean RSD	Analyte	n	# < LOD	# NC	# > LOD	mean RSD
Arsenic	3	3	0	0	---	Arsenic	3	3	0	0	---
Bromine	3	1	0	2	12.3%	Bromine	3	1	0	2	18.2%
Cadmium	3	2	0	1	40.5%	Cadmium	3	0	1	2	13.4%
Cobalt	3	2	0	1	7.0%	Cobalt	3	3	0	0	---
Mercury	3	3	0	0	---	Mercury	3	3	0	0	---
Molybdenum	3	3	0	0	---	Molybdenum	3	3	0	0	---
Lead	3	2	0	1	2.0%	Lead	3	0	0	3	4.3%
Antimony	3	2	0	1	4.9%	Antimony	3	1	0	2	6.7%

RSD: relative standard deviation.
#<LOD: number of cases where all measurements were below the detection limit.
#NC: number of cases where at least one of the measurements were below detection limits.
#> LOD: number of cases where all measurements were above the detection limit.

Table 7. Relative Standard Deviations (RSDs) in Triplicate Screenings of Plastic Products.

Plastics Triplicate Samples - Handheld						Plastics Triplicate Samples - Stand					
Analyte	n	# < LOD	# NC	# > LOD	mean RSD	Analyte	n	# < LOD	# NC	# >LOD	mean RSD
Arsenic	21	12	4	5	7.8%	Arsenic	21	18	1	2	10.7%
Bromine	21	2	2	17	7.9%	Bromine	21	5	5	10	4.0%
Cadmium	21	17	1	3	16.5%	Cadmium	21	15	1	5	14.7%
Cobalt	21	17	1	3	25.7%	Cobalt	21	21	0	0	---
Mercury	21	21	0	0	---	Mercury	21	21	0	0	---
Lead	21	13	1	7	9.3%	Lead	21	14	0	7	9.7%
Antimony	21	9	3	9	8.4%	Antimony	21	10	1	10	10.7%

#<LOD: number of cases where all measurements were below the detection limit.
#NC: number of cases where at least one of the measurements were below detection limits.
#> LOD: number of cases where all measurements were above the detection limit.

Standards

In addition to comparison with laboratory results, XRF accuracy was assessed through reference samples provided by the XRF manufacturer. Reference samples consisted of metal and polyethylene disks. The metal and plastic reference standards were measured 51 and 48 times, respectively, throughout the project. The known concentration of the reference samples along with XRF results are shown in tables 8 and 9.

Table 8. XRF Measurements of Standards in Metal Matrix (ppm).

Element	n	Standard conc.	XRF mean conc.	SD	RSD
Silver	51	29000	29431	321	1.1%
Cadmium	51	3300	3361	189	5.6%
Lead	51	1400	1919	149	7.7%
Copper	51	5000	4745	339	7.1%

SD: standard deviation; RSD: relative standard deviation

Table 9. XRF Measurements of Standards in Plastic Matrix (ppm).

Element	n	Standard conc.	Estimated error of Standard (95% CI) mg/kg	XRF mean conc.	SD	RSD
Bromine	48	501	± 20	466	8	1.8%
Cadmium	48	150	± 6	143	8	5.9%
Mercury	48	999	± 40	858	19	2.2%
Lead	48	1000	± 40	967	17	1.8%
Chromium	48	1000	± 40	905	72	7.9%

CI: confidence interval; SD: standard deviation; RSD: relative standard deviation

Mean RSD values were less than 10% for all elements in both matrices indicating good accuracy. Lead in the plastic standard was the only element to measure within the 95% confidence interval of the standard value. Confidence intervals were not provided with the metal standard.

XRF vs. Lab - Metals

Laboratory Results

Seventy-two individual components isolated from children's products were selected for laboratory analysis of metal analytes (arsenic, cadmium, cobalt, mercury, molybdenum, lead, and antimony). Fifty-seven of the samples were digested using the "plastics" method 3052 with microwave assist, and consisted of plastics, rubber, and textiles. The other fifteen samples were digested as "metal" products by method 3050B (leaching), which are not comparable to XRF readings. Tables 10 and 11 display statistical summaries of detected results for the plastic and metal products, respectively. The following summary includes only values above the laboratory detection limits, which varied but were typically less than 0.5 ppm.

Table 10. Statistical Summary of Detected Laboratory Results for Analysis of Plastics Products*.

Plastics Statistics	Arsenic (ppm)	Cadmium (ppm)	Cobalt (ppm)	Mercury** (ppm)	Molybdenum (ppm)	Lead (ppm)	Antimony (ppm)
% > LOD	53%	49%	46%	23%	21%	89%	74%
Minimum	0.11	0.04	0.12	0.01	0.35	0.21	0.76
25th Percentile	0.85	0.61	0.55	0.01	0.72	0.65	18.0
Median	2.05	6.90	1.44	0.01	1.70	3.15	95.1
Mean	436	133	25.0	0.04	20.0	432	763
75th Percentile	10.0	29.8	7.37	0.06	2.86	123	200
Maximum	7840	2860	237	0.13	191	7470	16300

*Plastic products include all non-metal matrices and were prepared for ICP-MS analysis following EPA Method 3052 (less hydrofluoric acid).

**The digestion method for mercury in all matrices was a leaching method, EPA 245.5.

Table 11. Statistical Summary of Detected Laboratory Results for Analysis of Metal Products*.

Metals Statistics	Arsenic (ppm)	Cadmium (ppm)	Cobalt (ppm)	Mercury** (ppm)	Molybdenum (ppm)	Lead (ppm)	Antimony (ppm)
% > LOD	26%	16%	21%	11%	11%	26%	19%
Minimum	6.53	0.11	0.10	0.01	5.11	0.24	0.20
25th Percentile	16.2	1.37	0.35	0.01	7.93	1.17	0.63
Median	17.6	7.42	21.0	0.03	22.4	18.3	2.10
Mean	45.6	544	32.1	0.03	23.4	7960	652
75th Percentile	44.6	13.8	49.9	0.05	39.8	111	25.6
Maximum	236	4830	106	0.08	41.8	90800	5470

*Metal products include only samples consisting of metal materials; these samples were prepared for analysis following EPA Method 3050B, which is a leaching test and not directly comparable to XRF data.

**Mercury preparation followed EPA Method 245.5.

XRF Comparison to Laboratory Metals Results

The following section compares XRF results using the four different types of measurement – 30-second initial screening, 60-second handheld, 60-second in-stand, and 60-second cryoground – to laboratory analysis results. The following comparisons include only the 57 samples consisting of non-metal material (plastics, foams, rubber, and textiles). Non-metal materials were digested using method 3052 that results in complete decomposition of the sample and is comparable to XRF readings. The 15 metal material samples were prepared for laboratory analysis using a leaching method and are therefore not comparable to XRF data and are excluded from the following analysis.

Complete results of XRF measurements and lab results for arsenic, antimony, cadmium, cobalt, lead, mercury, and molybdenum are included in Appendix F.

False Positives and Negatives

A concern of using XRF is whether the gun erroneously indicates that a contaminant is present when in fact it is not (false positive) or vice versa (false negative). Each of the four XRF screening methods was compared to laboratory results to determine the frequency at which false readings occurred. A false positive was defined whereby the XRF gun recorded a value greater than the LOD when the laboratory result was less than 5 ppm. A false negative occurred when the XRF reading was less than LOD, but the laboratory measurement was greater than the XRF's detection limit. Table 12 displays the number and percentage of XRF readings that were determined to be false positives or false negatives by comparison with the laboratory data.

With the exception of antimony, a sizeable percentage of the initial screening results for each of the elements were false positives. During the 60-second handheld screening on isolated materials, false positives were present in arsenic, cadmium, cobalt, and lead screenings. No false positives were recorded for the powder screening and only 1 measurement was determined to be a false positive for the 60-second stand reading.

After material isolation, the percentage of results as false positives was greatly reduced; this suggests that interfering materials may result in false positives when components are measured intact with the original product. False negatives were not as problematic. Only 3 false negatives occurred between all elements and analysis types.

The initial screening false positives were not necessarily low concentrations near detection limits. Figure 5 shows the concentrations recorded by XRF which were determined to be false positives.

Median initial screening false positive values were above 100 ppm for each of the elements except arsenic and cadmium. The high concentrations of false positive measurements suggest that interferences may be responsible for the inaccurate readings.

Table 12. False Positive and False Negative Results for Each XRF Screening Method.

XRF Method	# Analyzed	# > LOD	# False Positives	% False Positive	# False Negatives	% False Negative
	Lead					
Initial Screening	57	26	7	27%	0	0%
60s Hand	50	18	2	11%	1	6%
60s Stand	55	20	0	0%	0	0%
Powder	20	10	0	0%	0	0%
	Arsenic					
Initial Screening	57	14	6	43%	0	0%
60s Hand	50	9	4	44%	0	0%
60s Stand	55	10	1	10%	0	0%
Powder	20	6	0	0%	0	0%
	Cobalt					
Initial Screening	57	8	6	75%	1	13%
60s Hand	50	3	1	33%	0	0%
60s Stand	55	5	0	0%	0	0%
Powder	20	3	0	0%	0	0%
	Cadmium					
Initial Screening	57	19	8	42%	1	5%
60s Hand	50	10	1	10%	0	0%
60s Stand	55	10	0	0%	0	0%
Powder	20	3	0	0%	0	0%
	Mercury					
Initial Screening	57	1	1	100%	0	0%
60s Hand	50	0	0	-	0	-
60s Stand	55	0	0	-	0	-
Powder	20	0	0	-	0	-
	Antimony					
Initial Screening	57	34	2	6%	0	0%
60s Hand	50	26	0	0%	0	0%
60s Stand	55	30	0	0%	0	0%
Powder	20	8	0	0%	0	0%

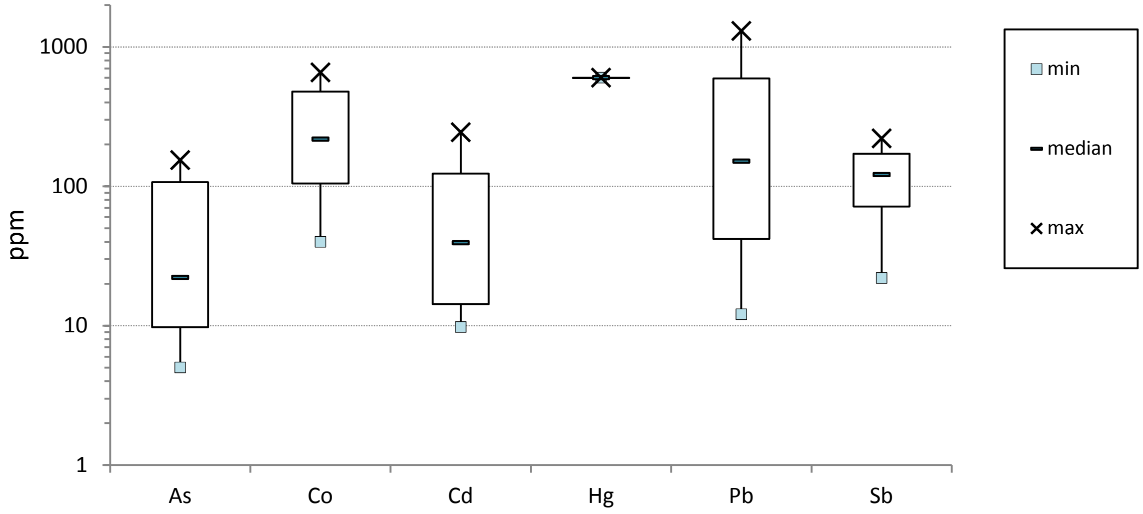

Figure 4. Box-plot Displaying Initial Screening XRF Results Determined as False Positives.
Y axis is logarithmic scale.
Top and bottom lines of rectangles represent 75th and 25th percentiles, respectively.

Regressions between Methods

Simple linear regressions were constructed for each element to evaluate relationships between laboratory results and the 4 different XRF screening methods. False positives and false negatives were included in the dataset for regressions. Where a measurement was not detected, half of the LOD was used. Data was $\log_{10}$ transformed prior to regression analysis to improve normality of the data. Table 13 displays r^2 values on $\log_{10}$ normalized data for each of the XRF reading methods. Figure 6 presents regressions on $\log_{10}$ normalized values for the initial 30-second screening. Tables and Figures displaying full regression results for each of the XRF measurement types are included in Appendix D.

Table 13. Linear Regression Results for XRF and Laboratory Measurements ($\log_{10}$ normalized values).

XRF method	Arsenic		Cadmium		Cobalt		Lead		Antimony	
	r^2 (n)	p-value	r^2 (n)	p-value	r^2 (n)	p-value	r^2 (n)	p-value	r^2 (n)	p-value
Initial screening	**.72 (14)**	<0.001	**.28 (20)**	0.016	0.12 (8)	0.401	**.44 (26)**	<0.001	**.46 (34)**	<0.001
60s hand	.09 (9)	0.445	**.53 (10)**	0.017	0.99 (3)	0.060	**.80 (19)**	<0.001	**.90 (26)**	<0.001
60s stand	**.54 (10)**	0.015	**.69 (10)**	0.003	**.99 (5)**	<0.001	**.93 (20)**	<0.001	**.84 (30)**	<0.001
Powder	**.96 (6)**	<0.001	**1 (3)**	0.024	.99 (3)	0.061	**.99 (10)**	<0.001	**.97 (8)**	<0.001

Bolded values indicate statistically significant relationship at alpha = 0.05.

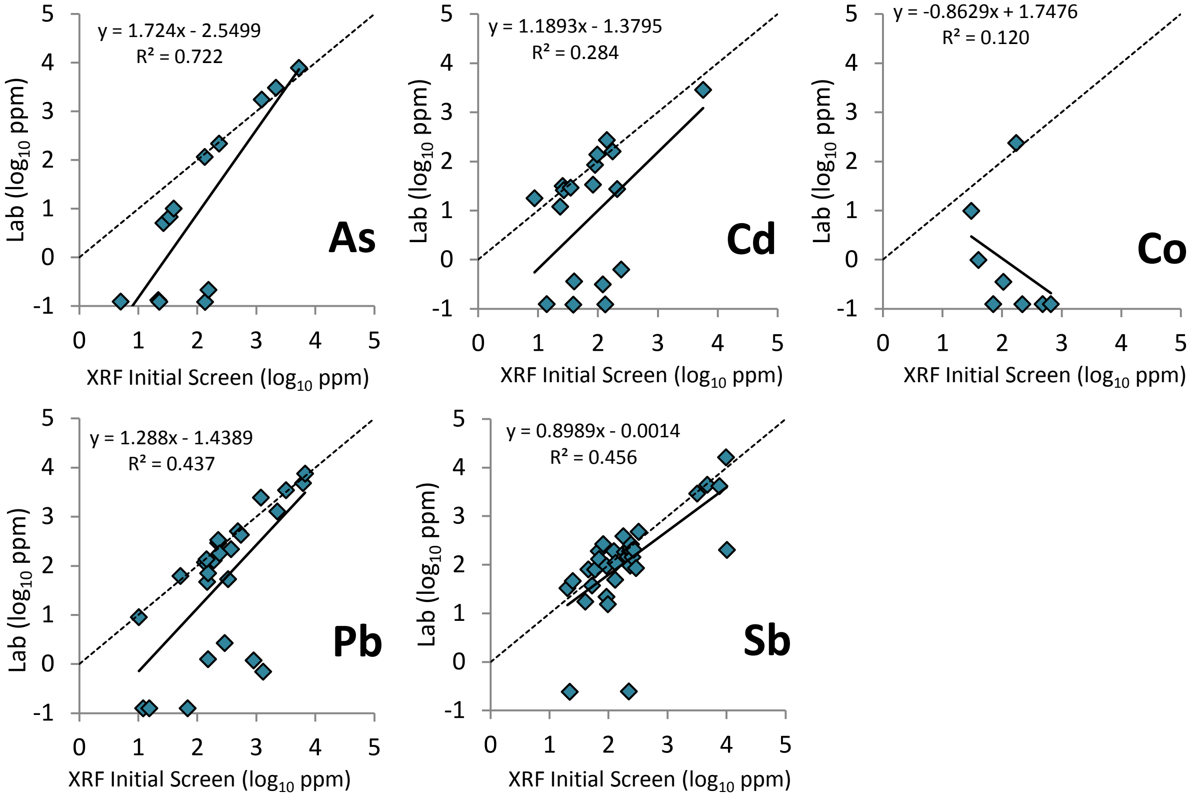

Figure 5. Linear Regression Plots between Initial XRF 30-second Hand Screening and Laboratory Results ($\log_{10}$ normalized values).

Dashed line indicates line of equality, solid lines indicate regression trendline.

Linear regressions on normalized data indicate that XRF and laboratory measurements correlated well when materials were isolated. The initial screening regressions showed weak relationships, primarily due to false positives (Figure 6). When false positives were removed from the dataset, the initial screening relationships were much stronger, ranging in r^2 from 0.67 – 0.99 (data not shown). Regression coefficient values generally increased as materials were isolated and the analysis further refined (i.e., measured in stand or as powder). XRF readings on isolated components compared well with laboratory results, with linear regression coefficients typically greater than 0.90. Lead and antimony XRF readings correlated particularly well with lab results, and regression lines were close to the line of equality (see Appendix D).

RPDs between Methods

The distribution of relative percent differences (RPDs) between sample-specific XRF and laboratory measurements (non-transformed ppm) for each of the XRF screening methods are provided in Figure 7. False positives and false negatives were included in the RPD calculations and non-detects were set to half of the detection limit.

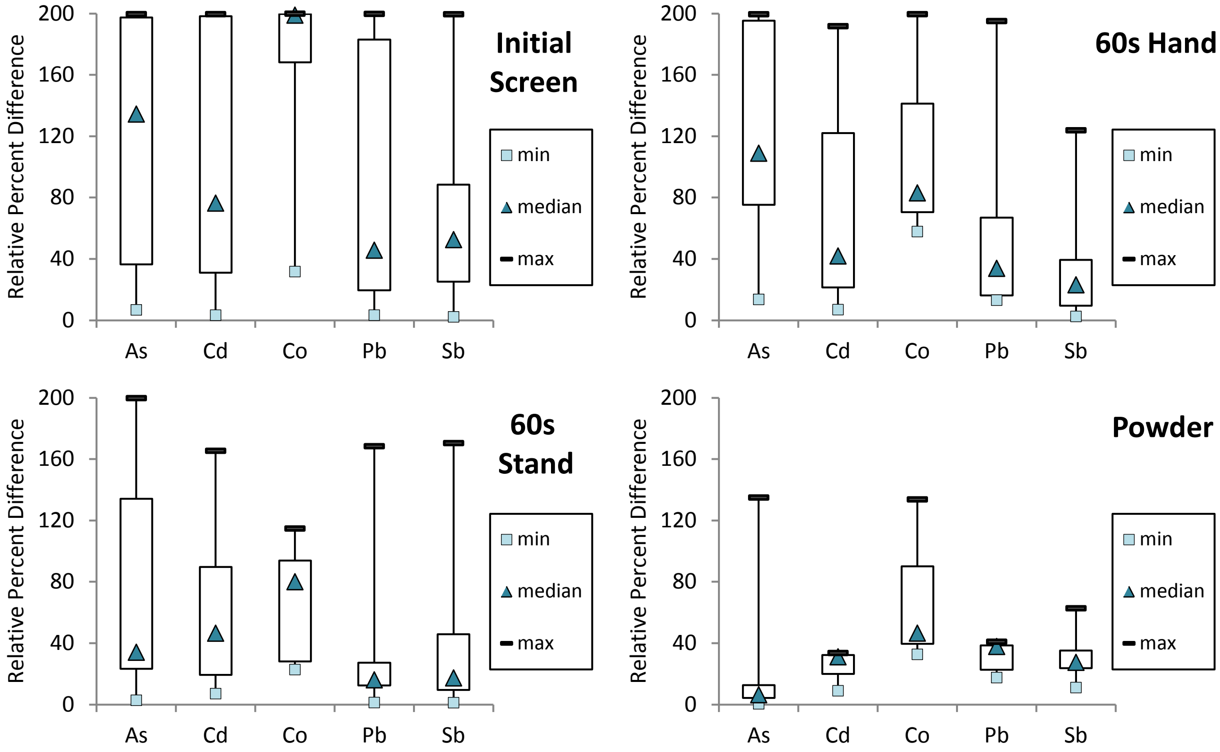

Figure 6. Minimum, Maximum, and Interquartile Ranges of Relative Percent Differences (RPDs) between Laboratory Measurements and XRF Screening Methods.
Top and bottom lines of rectangles represent 75th and 25th percentiles, respectively.

In general, RPDs were highest for the initial screening and lowest for the 60-second in-stand and powder measurements. Similar to regressions, RPDs for each element decreased with material isolation and use of the stand. Median RPDs were particularly high for cobalt measurements (47-199%). Powder screenings of arsenic and in-stand 60-second measurements of lead and antimony had the best agreement with lab results (median RPD = 6%, 16%, and 17%, respectively).

XRF as a Screening Tool for CSPA metals

Detection limits achieved by the XRF analyzer varied greatly depending on sample material, but LODs were generally well below 100 ppm for plastic matrices. The XRF performed reasonably well in precision and accuracy tests on isolated materials for antimony, arsenic, cadmium, cobalt, lead, and mercury.

The comparison of XRF data to laboratory results was limited to only non-metal matrices (57 samples). A number of false positives occurred using the 30-second initial screening measurements of non-metal product samples. False positives were greatly decreased by isolating the component of interest and measuring in a stand. Very few false negatives occurred for any of the XRF measurement methods. While the XRF can be used to screen new products, it is recommended that the item be deconstructed and re-measured to confirm the original analysis.

XRF vs. Lab - PBDEs

Laboratory Results

A statistical summary of initial screening XRF results for bromine measurements is presented in a previous section, *XRF Screening Results*, on page 20.

Sixty-eight samples were analyzed for 6 PBDE congeners (-47, -99, -100, -154, -153, -209) by RIAL Laboratory. Samples were chosen for laboratory analysis based on a range of XRF-measured bromine concentrations. Fourteen of the samples consisted of recycled electronics and one foam sample from a couch manufactured in the early 1990s. The remaining 54 samples were collected from new children's products. Laboratory detection limits were typically less than 0.5 ppm for all congeners except BDE-209 where they were generally less than 5 ppm. Table 14 displays statistical summaries of detected results for the children's products and electronics/foams.

Table 14. Statistical Summary of >LOD Laboratory PBDE Results.

	Children's Items ∑PBDEs (ppm)	Recycled electronics/ old foams ∑PBDEs (ppm)
% > LOD	22%*	93%
Minimum	0.6	33
25th Percentile	2.1	63
Median	8.5	120
Mean	153.4	1433
75th Percentile	110.3	250
Maximum	902.4	15140

*12 samples were detected > LOD.
Five of the samples were qualified NJ.
These samples contained RPD > 40% between columns on the ECD analysis and were not confirmed by GCMS.

PBDEs were infrequently detected in the children's products at low levels. Only one sample, a plastic necklace chain, contained PBDEs greater than 500 ppm. No samples of new products were above the 1000 ppm PBDE threshold outlined in the states PBDE ban (Ecology, 2008).

Each of the recycled electronics and foam samples contained measurable amounts of PBDEs except one sample. With the exception of two recycled electronics samples, all were below 1000 ppm.

XRF Bromine Comparison to PBDE Results

Previous researchers have identified a relationship between XRF-measured bromine and laboratory-measured PBDEs in consumer products (Allen et al, 2008; Imm et al, 2009; Stapleton et al, 2011). Because we tested primarily children's products that have not historically used PBDEs as flame retardants, it is unlikely any correlation would be found for children's products in this study. However, to investigate this relationship, we compared bromine detections with PBDE detections, and constructed linear regressions and RPDs in a similar manner to the metals portion of the study. Complete results of XRF-measured bromine and laboratory PBDEs are included in Appendix F.

Comparison of Bromine and PBDE Detections

Detections of bromine measured by XRF were compared to detections of PBDEs by the laboratory. The authors acknowledge that bromine can be present in products in which PBDEs are absent. Our goal, however, was to examine how often the XRF read bromine when PBDEs were present and vice versa. A comparison of bromine and PBDE detections is displayed in Table 15.

Table 15. Comparison of Bromine and PBDE Detections.

XRF Method	# Analyzed	# Samples >LOD Br	# Br detected in absence of PBDEs	% Samples Br detected in absence of PBDEs	# PBDEs detected in absence of Br	% samples PBDEs detected in absence of Br
Initial Screening	68	56	33	59%	0	0%
60s Hand	64	57	37	65%	0	0%
60s Stand	67	45	26	58%	0	0%
Powder	42	30	11	37%	0	0%

The majority of samples with XRF-measured bromine detections did not contain PBDEs. The percentage of samples with bromine measurements in absence of PBDEs was even greater (67%) when recycled electronics/old foams were removed from the dataset, leaving only children's products. There were no cases where the XRF analyzer did not detect bromine but PBDEs were present.

Bromine was the most common element detected in the screening process (40.7%), yet presence of PBDEs was isolated to a few samples. Of the 1178 initial screening XRF measurements, 17 components (from 12 different children's products) contained bromine concentrations above 1000 ppm. Twelve of these samples were included in those sent to the laboratory and only four contained PBDEs above the detection limit (Figure 8).

Foam from kid's furniture contained the highest concentrations of XRF-measured bromine (around 2%, or 20000 ppm). However, total PBDEs were not quantified above 1 ppm in any of the foam samples. Two of the plastic samples contained higher PBDE levels (429 and 902 ppm), but PBDE content was a small fraction of the total XRF bromine value. As PBDEs typically are found in the 7-14% level when used as a flame retardant, it is unlikely these levels are due to their use as a flame retardant.

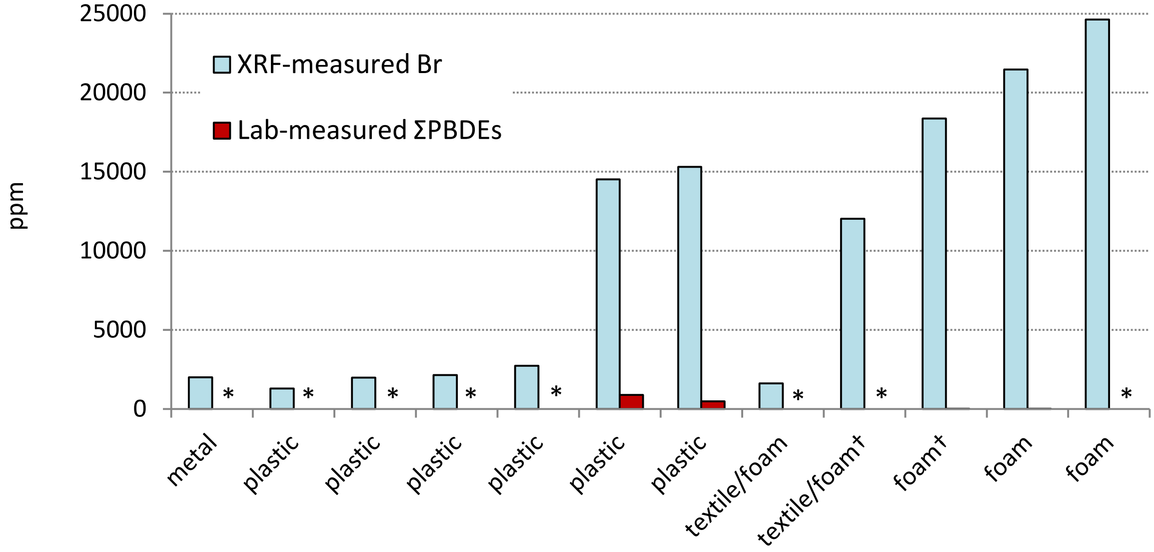

Figure 7. XRF-measured Bromine and Laboratory-quantified Total PBDEs in Children's Products with >1000 ppm XRF Bromine.

*A * symbol denotes the lab sample was below detection limits.*
† indicates the two samples were separate components of the same original product.

Other studies have encountered false positives when comparing XRF-measured bromine to PBDEs. Stapleton et al. (2011) measured bromine in baby product foams by XRF and found several samples lacking PBDEs. The authors suggested that the false positives occurred due to matrix interferences or the presence of unknown brominated compounds. The study also quantified a commercial mixture that contains the brominated compounds TBB[1] and TBPH[2] (Firemaster 550) in several sample foams that had tested positive for bromine. Other non-PBDE brominated flame retardants including DBDPE[3], BTBPE[4], and PBBs[5] have been measured in children's toys collected in Southern China (Chen et al., 2009).

Among the recycled electronics sent to the laboratory for PBDE analysis, one sample contained XRF-measured bromine but no laboratory-measured PBDEs. Allen et al. (2008) discovered false positives in three computer monitor samples when using XRF-measured bromine as a surrogate for PBDE concentrations. The study found another brominated flame retardant, TBBPA[6], was responsible for the bromine measured by XRF when PBDEs were absent.

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[1] TBB: 2-ethylhexyl-2,3,4,5-tetrabromobenzoate
[2] TBPH: bis(2-ethylhexyl)-2,3,4,5-tetrabromophthalate
[3] DBDPE: decabromodiphenyl ethane
[4] BTBPE: 1,2-bis(2,4,6-tribromophenoxy)ethane
[5] PBBs: polybrominated biphenyls
[6] TBBPA: tetrabromobisphenol A

Regressions between Methods

Least squares linear regressions were constructed to assess relationships between XRF-measured bromine results and laboratory PBDE results. Only samples where both XRF-measured bromine and PBDE values were greater than detection limits were included in regressions. Regressions were computed on $\log_{10}$ normalized values for improved normality of the data. Table 16 displays linear regression coefficients for each of the XRF methods. Figure 9 shows regression charts for each of the screening methods. Linear regression results on raw values are presented in Appendix D.

Table 16. Linear Regression Results for XRF-Measured Bromine and Laboratory PBDE Results.

Log_{10}-normalized		
XRF method	Br/PBDEs	
	r^2 (n)	p-value
Initial screening	0.16 (23)	0.059
60s hand	**0.27 (23)**	**0.012**
60s stand	0.15 (23)	0.073
Powder	**0.48 (19)**	**0.001**

Bolded values indicate significant relationship at alpha = 0.05.

Weak positive relationships were apparent for each of the screening methods. The relationships were significant for the 60-second handheld and powder methods, but all r^2 values were less than 0.50. Using non-transformed ppm values, no relationship existed between XRF-measured bromine and PBDEs (r2 < 0.1; Appendix F). As the regression charts show, bromine measured by XRF was not a useful predictor of PBDE concentrations in the samples analyzed.

Recycled electronics samples did not show a relationship between bromine and PBDEs when analyzed separately ($r^2 < 0.1$ for all screening measures). Other studies have found strong relationships between XRF-measured bromine and PBDEs in electronic housings (Allen et al., 2008). However, Suzuki et al. (2009) reported poor correlations between bromine concentrations measured by micro-XRF spectrometry and PBDE concentrations in indoor dust, citing other brominated flame retardants, such as TBBPA, HBCD[7], and TBPh[8], were the likely source of bromine.

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[7] HBCD: hexabromocyclododecane

[8] TBPh: 2,4,6-tribromophenol

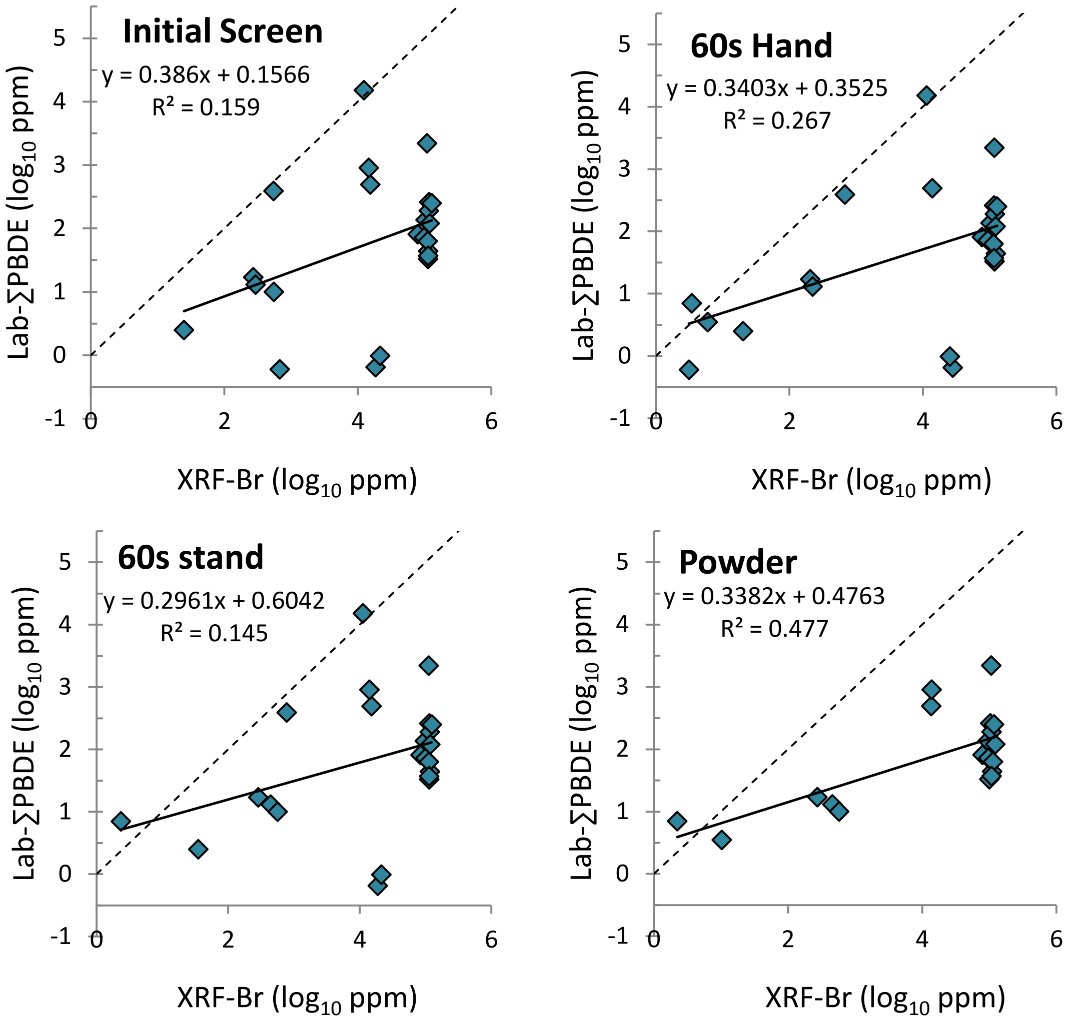

Figure 8. Linear Regression Plot Between Log_{10} Normalized Values for XRF-Measured Bromine and Laboratory PBDE Results.

Dashed line indicates line of equality, solid lines indicate regression trendline.

RPDs between Methods

The distribution of sample-specific relative percent differences (RPDs) between XRF-measured bromine and laboratory PBDE results for each of the XRF screening methods are provided in Figure 9. Only samples with detections of both XRF-bromine and PBDEs were included in RPD calculations.

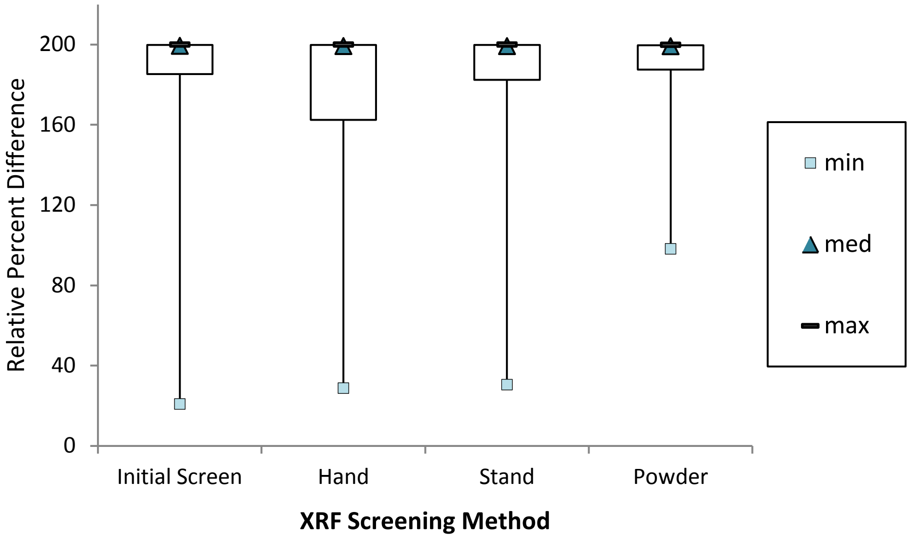

Figure 9. Distribution of Relative Percent Differences Between XRF-Measured Bromine and PBDE Laboratory Results.

Top and bottom lines of rectangles represent 75th and 25th percentiles, respectively.

The interquartile range was well above 150 RPD for all XRF screening methods. The median, 75th percentile, and maximum RPDs were all near 200% which is the limit of the RPD formula. Relative percent differences were below 50% in only two samples – a furniture foam from the 1990s and a children's product containing textile and foam. With the exception of these two samples, almost all of the bromine recorded by XRF was not associated with PBDEs.

XRF as a Screening Tool for PBDEs

The majority of samples with XRF-measured bromine did not contain PBDEs. When both bromine and PBDEs were present, significant but poor relationships ($r^2 < 0.50$) were evident for log-normalized XRF-measured bromine and PBDEs using the 60 second hand measurement and the powder measurement on isolated products. No significant regressions were evident using non-transformed values. The majority of relative percent differences between XRF-measured bromine and PBDEs were near 200%, with bromine present in levels much higher than PBDEs. Because no samples were found to contain PBDEs in absence of XRF-measured bromine, XRF methods may be a useful tool in screening products that *could* contain PBDEs. However, as expected and based on the lack of relationship between PBDEs and XRF bromine, laboratory analysis would be required for any determination of PBDEs.

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Conclusions

A total of 316 new children's products and 36 recycled electronics parts were analyzed by XRF for concentrations of antimony, arsenic, cadmium, cobalt, lead, mercury, molybdenum, and bromine. Laboratory measurements on a subset of the products were compared to several types of XRF screening methods in order to examine the efficacy of XRF as a screening tool for metal analytes (n = 57) and PBDEs (n = 68).

In plastic products, limit of detections (LODs) achieved by the XRF analyzer were generally below the 100 ppm reporting threshold for contaminants in children's products. Minimum LODs for plastic samples were less than 10 ppm for all elements except for cobalt (17 ppm) and antimony (13 ppm). Measurements on metal matrices did not achieve median LODs below 100 ppm for any of the elements except for bromine and cadmium. For metal matrices, minimum LODs were more variable and ranged from 4 – 75 ppm.

Linear regressions between XRF measurements and laboratory results for metal analytes showed good agreement, with r^2 typically greater than 0.90 when the components of interest were isolated from the rest of the product. Measuring products without first isolating the component of interest produced a large amount of false positives for the metal analytes. False negatives were not as problematic, with only three false negative readings occurring between all screening methods and elements analyzed.

The majority of samples with XRF-measured bromine did not contain PBDEs above detection limits. Results of XRF measurements showed high concentrations of bromine in foam from several pieces of children's furniture (around 2%, or 20,000 ppm). These products did not contain PBDEs above 1 ppm. No product forwarded to the lab contained PBDEs above 1000 ppm.

When both bromine and PBDEs were present, poor relationships ($r^2 < 0.50$) and high sample-specific relative percent differences were found. PBDEs represented a very small fraction of the total bromine present.

Recommendations

As a result of the study the following recommendations are made:

- For analysis of antimony, arsenic, cadmium, cobalt, lead, and mercury in non-metal matrices the XRF analyzer may provide adequate data for screening purposes. However, due to the occurrence of false positives, the authors recommend material isolation and use of a stand to avoid interferences. If the XRF analyzer is used for handheld screening on intact products, specific materials of interest should be isolated from detected products and re-measured in a stand to confirm the original analysis.

- Because there were no samples where PBDEs were detected in absence of XRF-measured bromine, XRF may be useful as a screening tool to identify samples that *could* contain PBDEs. As expected, the lack of relationship between XRF-measured bromine and laboratory-measured PBDEs indicate that laboratory testing would be necessary for determination of PBDEs in samples. Additional study is needed to determine if XRF-measured bromine could be useful as a screening tool for other brominated flame retardants.

- For laboratory analysis of antimony, arsenic, cadmium, cobalt, lead, and molybdenum, all samples should be digested using EPA Method 3052 to achieve total decomposition of the samples. Research should be done to find laboratories which can digest metal matrices using this method (microwave-assisted).

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Appendices

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Appendix A. Glossary, Acronyms, and Abbreviations

Glossary

Cryogenic:	Of or relating to very low temperatures.
Cryomilled:	The process of reducing a sample to very small particle sizes by employing cryogenic temperatures and a mechanical mill.
Niton's TestAll®:	A Thermo Scientific Niton XRF analyzer setting in which the analyzer performs a pre-measurement check to identify the type of sample being screened. The XRF analyzer will determine whether the sample is a metal, mineral, plastic, or painted object and select the correct mode automatically.

Acronyms and Abbreviations

Following are acronyms and abbreviations used frequently in this report.

Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
LOD	Limit of Detection
MEL	Manchester Environmental Laboratory
PBDE	polybrominated diphenyl ethers
PBT	persistent, bioaccumulative, and toxic substance
RIAL	Rhode Island Analytical
RPD	Relative percent difference
RSD	Relative standard deviation
SOP	Standard operating procedures
SRM	Standard reference materials
WAC	Washington Administrative Code
XRF	X-ray fluorescence

Metals

Ag	Silver
As	Arsenic
Br	Bromine
Cd	Cadmium
Co	Cobalt
Hg	Mercury
Mo	Molybdenum
Pb	Lead
Sb	Antimony

Units of Measurement

g	gram, a unit of mass
mg	milligrams
mg/Kg	milligrams per kilogram (parts per million)
ng/g	nanograms per gram (parts per billion)
ug /g	micrograms per gram (parts per million)
ug/Kg	micrograms per kilogram (parts per billion)
ug /L	micrograms per liter (parts per billion)

Appendix B. Quality Assurance/Quality Control Results

Metals

Table B-1. LCS Recoveries.

Arsenic	%	Antimony	%	Cadmium	%
B11D141-BS1	106	B11E058-BS2	95	B11E012-BS1	99
B11E017-BS1	101	B11E058-BS1	95	B11E058-BS1	103
B11E112-BS1	113	B11D111-BS1	102	B11D111-BS1	98
B11D090-BS1	101	B11D159-BS1	95	B11D159-BS1	96
B11E012-BS1	100	B11E112-BS1	101	B11E017-BS1	96
B11D111-BS1	102	B11E012-BS1	95	B11E058-BS2	103
B11D159-BS1	99	B11E017-BS1	96	B11D141-BS1	99
B11E058-BS2	104	B11D090-BS1	101	B11D090-BS1	100
B11E058-BS1	104	B11D141-BS1	96	B11E112-BS1	113

Cobalt		Lead		Mercury	
B11D141-BS1	97	B11D111-BS1	100	B11E049-BS1	92
B11D159-BS1	95	B11D141-BS1	104	B11E011-BS1	96
B11D111-BS1	95	B11D090-BS1	104	B11D182-BS1	97
B11E058-BS1	108	B11E012-BS1	103	B11D155-BS1	93
B11E012-BS1	95	B11E112-BS1	104	B11D070-BS1	95
B11E017-BS1	99	B11D159-BS1	96		
B11E058-BS2	108	B11E017-BS1	101		
B11D090-BS1	102	B11E058-BS2	105		
B11E112-BS1	103	B11E058-BS1	106		

Molybdenium	
B11D159-BS1	98
B11D141-BS1	92
B11D111-BS1	100
B11D090-BS1	99
B11E058-BS2	99
B11E058-BS1	99
B11E012-BS1	99
B11E112-BS1	98
B11E017-BS1	99

Table B-2. LCS/LCS duplicates RPD.

Arsenic	%	Antimony	%	Cadmium	%
B11E112-BSD1	2	B11E112-BSD1	1	B11E112-BSD1	0.9

Cobalt		Lead		Molybdenium	
B11E112-BSD1	0.1	B11E112-BSD1	2	B11E112-BSD1	2

Table B-3. LCS recoveries - HF digestion.

Sample #	Analyte	%
B110931-BS2	As	95
B110930-BS2	Cd	90
B110930-BS2	Co	95
B110930-BS2	Mo	93
B110930-BS2	Pb	95
B110930-BS2	Sb	85

Table B-4. Laboratory blanks.

Antimony			Arsenic			Cadmium		
B11D111-BLK1	0.265		B11D141-BLK1	0.1	U	B11E012-BLK1	0.25	U
B11D159-BLK1	0.5	U	B11E112-BLK1	0.5	U	B11E017-BLK1	0.25	U
B11E012-BLK1	0.5	U	B11D090-BLK1	0.25	U	B11E058-BLK1	0.00002	U
B11E017-BLK1	0.5	U	B11E012-BLK1	0.25	U	B11D159-BLK1	0.25	U
B11E112-BLK1	1	U	B11E017-BLK1	0.25	U	B11D111-BLK1	0.1	U
B11E058-BLK1	0.0002	U	B11D111-BLK1	0.1	U	B11D141-BLK1	0.1	U
B11D090-BLK1	0.5	U	B11D159-BLK1	0.25	U	B11D090-BLK1	0.25	U
B11D141-BLK1	0.2	U	B11E058-BLK1	0.0001	U	B11E112-BLK1	0.5	U

Cobalt			Lead			Mercury		
B11E012-BLK1	0.25	U	B11D111-BLK1	0.568		B11E049-BLK1	0.005	U
B11E017-BLK1	0.25	U	B11D141-BLK1	0.177		B11E011-BLK1	0.005	U
B11D141-BLK1	0.1	U	B11D090-BLK1	0.25	U	B11D182-BLK1	0.005	U
B11D111-BLK1	0.1	U	B11E017-BLK1	0.25	U	B11D070-BLK1	0.005	U
B11D159-BLK1	0.25	U	B11E112-BLK1	0.5	U	B11D155-BLK1	0.005	U
B11E058-BLK1	0.0001	U	B11E012-BLK1	0.25	U			
B11D090-BLK1	0.25	U	B11D159-BLK1	0.25	U			
B11E112-BLK1	0.5	U	B11E058-BLK1	2E-05	U			

Molybdenum		
B11D141-BLK1	0.5	U
B11D090-BLK1	0.25	U
B11E058-BLK1	0.0001	U
B11D159-BLK1	0.25	U
B11D111-BLK1	0.1	U
B11E112-BLK1	0.5	U
B11E017-BLK1	0.25	U
B11E012-BLK1	0.25	U

U = undetected at level indicated.

Table B-5. Lab Blanks HF digestion.

Antimony			Arsenic			Cadmium		
Sample #	Result		Sample #	Result		Sample #	Result	
B110930-BLK1	0.04	U	B110931-BLK1	0.1	U	B110930-BLK1	0.02	U
B110930-BLK2	0.04	U	B110931-BLK2	0.1	U	B110930-BLK2	0.02	U
B110930-BLK3	0.04	U	B110931-BLK3	0.1	U	B110930-BLK3	0.02	U
B110930-BLK4	0.04	U	B110931-BLK4	0.1	U	B110930-BLK4	0.02	U

Cobalt			Lead			Molybdenum		
Sample #	Result		Sample #	Result		Sample #	Result	
B110930-BLK1	0.05	U	B110930-BLK1	0	U	B110930-BLK1	0.1	U
B110930-BLK2	0.05	U	B110930-BLK2	0	U	B110930-BLK2	0.1	U
B110930-BLK3	0.05	U	B110930-BLK3	0	U	B110930-BLK3	0.1	U
B110930-BLK4	0.05	U	B110930-BLK4	0	U	B110930-BLK4	0.1	U

U = undetected at level indicated.

Table B-6. Laboratory Duplicates.

Antimony	Duplicate (ppm)		Source (ppm)		RPD (%)	Arsenic	Duplicate (ppm)		Source (ppm)		RPD (%)
B11D159-DUP1	95.1		94.4		1	B11D141-DUP1	27.2		26.4		3
B11D111-DUP1	21400	J	16300	J	27	B11D090-DUP1	0.243	U	0.243	U	
B11E017-DUP1	0.5	U	0.498	U		B11E017-DUP1	0.25	J	0.306	J	20
B11E012-DUP1	182		183		1	B11E012-DUP1	1.11	J	1.23	J	10
B11D090-DUP1	0.485	U	0.485	U		B11D111-DUP1	4.87		4.06		18
B11D141-DUP1	2.44		2.57		5	B11D159-DUP1	1.49	J	1.23	J	19
Cadmium						Cobalt					
B11E017-DUP1	0.25	U	0.249	U		B11E017-DUP1	0.25	U	0.249	U	
B11E012-DUP1	1.24		1.22		2	B11D141-DUP1	44.6		43.3		3
B11D111-DUP1	0.099	U	0.097	U		B11E012-DUP1	1.63		1.5		8
B11D159-DUP1	17.8		17.8		0	B11D159-DUP1	1.5		1.44		4
B11D141-DUP1	0.092	U	0.097	U		B11D111-DUP1	0.342		0.354		3
B11D090-DUP1	0.243	U	0.243	U		B11D090-DUP1	0.243	U	0.243	U	
Lead						Mercury					
B11D141-DUP1	0.401	J	2.54	J	145	B11E011-DUP1	0.005	U	0.005	U	
B11D111-DUP1	6.1		0.097	U		B11D182-DUP1	0.0149		0.0147		1
B11D090-DUP1	2490		2430		2	B11D070-DUP1	0.0098	U	0.0103	U	
B11E017-DUP1	0.25	U	0.249	U		B11D155-DUP1	0.005	U	0.0051	U	
B11E012-DUP1	6.06		6.09		0						
B11D159-DUP1	7090		7470		5						
Molybdenum											
B11D141-DUP1	7.67		7.55		2						
B11D090-DUP1	34.3		33.9		1						
B11D159-DUP1	0.246	U	0.248	U							
B11D111-DUP1	0.099	U	0.097	U							
B11E017-DUP1	0.25	U	0.249	U							
B11E012-DUP1	0.249	U	0.246	U							

U = undetected at level indicated. J = report result is an estimate.

Table B-7. Laboratory duplicates - HF digestion.

Analyte	Duplicate (ppm)	Source (ppm)	RPD (%)
Arsenic	3071	3060	0.4%
Cadmium	29.05	31.6	8.4%
Cobalt	219.5	219	0.2%
Molybdenum	6.23	6.29	1.0%
Lead	129.3	135	4.3%
Antimony	77.24	79.5	2.9%

Table B-8. Matrix Spike Recoveries.

Antimony	%	Arsenic	%	Cadmium	%
B11D111-MS1	95	B11D141-MS1	106	B11D159-MS1	97
B11D159-MS1	94	B11E017-MS1	103	B11E017-MS1	102
B11E017-MS1	98	B11D090-MS1	106	B11E012-MS1	92
B11E012-MS1	491	B11E012-MS1	101	B11D111-MS1	95
B11D090-MS1	99	B11D159-MS1	100	B11D141-MS1	119
B11D141-MS1	103	B11D111-MS1	99	B11D090-MS1	97
Cobalt		Lead		Mercury	
B11E012-MS1	99	B11D141-MS1	92	B11E049-MS1	84
B11D159-MS1	93	B11D090-MS1	218	B11E011-MS1	86
B11D141-MS1	119	B11E017-MS1	101	B11D182-MS1	91
B11E017-MS1	98	B11E012-MS1	106	B11D155-MS1	84
B11D111-MS1	87	B11D159-MS1	94	B11D070-MS1	52
B11D090-MS1	105	B11D111-MS1	96		
Molybdenum					
B11D090-MS1	112				
B11D159-MS1	98				
B11D111-MS1	100				
B11D141-MS1	102				
B11E012-MS1	98				
B11E017-MS1	100				

Table B-9. Matrix Spike Duplicates RPD.

Antimony	%	Arsenic	%	Cadmium	%
B11D111-MS1/MSD1	1	B11D111-MS1/MSD1	1	B11D111-MS1/MSD1	0.8
B11D159-MS1/MSD1	0.3	B11D159-MS1/MSD1	0.3	B11D159-MS1/MSD1	2
B11E017-MS1/MSD1	0.3	B11E017-MS1/MSD1	2	B11E017-MS1/MSD1	0.09
B11E012-MS1/MSD1	3	B11E012-MS1/MSD1	0.8	B11E012-MS1/MSD1	3
B11D090-MS1/MSD1	5	B11D090-MS1/MSD1	0.8	B11D090-MS1/MSD1	2
B11D141-MS1/MSD1	3	B11D141-MS1/MSD1	2	B11D141-MS1/MSD1	0.2
Cobalt		Lead		Mercury	
B11D111-MS1/MSD1	4	B11D111-MS1/MSD1	0.7	B11E049-MS1/MSD1	5
B11D159-MS1/MSD1	4	B11D159-MS1/MSD1	3	B11E011-MS1/MSD1	3
B11E017-MS1/MSD1	2	B11E017-MS1/MSD1	3	B11D182-MS1/MSD1	3
B11E012-MS1/MSD1	7	B11E012-MS1/MSD1	5	B11D155-MS1/MSD1	4
B11D090-MS1/MSD1	4	B11D090-MS1/MSD1	3	B11D070-MS1/MSD1	31
B11D141-MS1/MSD1	2	B11D141-MS1/MSD1	0.6		
Molybdenum					
B11D111-MS1/MSD1	1				
B11D159-MS1/MSD1	4				
B11E017-MS1/MSD1	3				
B11E012-MS1/MSD1	11				
B11D090-MS1/MSD1	1				
B11D141-MS1/MSD1	3				

Table B-10. Matrix Spike Recoveries HF digestion and Duplicates HF digestion.

Sample #	Analyte	%
B110931-MS2	Arsenic	80
B110930-MS1	Cadmium	49
B110930-MS1	Cobalt	117
B110930-MS1	Molybdenum	91
B110930-MS1	Lead	90
B110930-MS1	Antimony	105

Table B-11. Matrix Spike Duplicates RPD.

Sample #	Analyte	%
B110930-MS1/MS2	Cadmium	69
B110930-MS1/MS2	Cobalt	11
B110930-MS1/MS2	Molybdenum	2.2
B110930-MS1/MS2	Lead	6.5
B110930-MS1/MS2	Antimony	19

PBDEs

Table B-12. LCS and LCS Duplicates.

	LCS Recoveries (%)								
	1104-06537-022	1104-06537-024	1104-06537-026	1104-06537-027	1104-06538-014	1104-06538-015	1104-06538-017	1104-06538-018	1104-06542-014
PBDE-047	86	70	75	89	75	89	90	94	86
PBDE-100	92	92	75	89	75	89	88	93	92
PBDE-099	85	71	73	86	73	86	87	92	85
PBDE-154	84	68	68	80	68	80	80	86	84
PBDE-153	80	64	67	76	67	76	77	83	80
PBDE-209	66	62	102	99	102	99	93	106	66

	LCS Recoveries (%)							
	1104-06539-014	1104-06540-017	1104-06540-018	1104-06540-020	1104-06541-004	1104-06541-005	1104-06542-011	1104-06542-012
PBDE-047	76	61	92	89	61	93	91	86
PBDE-100	68	74	116	92	74	116	98	93
PBDE-099	59	57	92	88	57	92	90	85
PBDE-154	59	53	86	86	53	86	88	84
PBDE-153	52	50.00	84	85	50	84	84	80
PBDE-209	40	84	116	155	84	116	158	172

	LCS Duplicates								
	1104-06537-026	1104-06537-027	RPD (%)	1104-06538-014	1104-06538-015	RPD (%)	1104-06538-017	1104-06538-018	RPD (%)
PBDE-047	75	89	17	75	89	17	90	94	4
PBDE-100	75	89	17	75	89	17	88	93	6
PBDE-099	73	86	16	73	86	16	87	92	6
PBDE-154	68	80	16	68	80	16	80	86	7
PBDE-153	67	76	13	67	76	13	77	83	8
PBDE-209	102	99	3	102	99	3	93	106	13

	LCS Duplicates								
	1104-06540-017	1104-06540-018	RPD (%)	1104-06541-004	1104-06541-005	RPD (%)	1104-06542-011	1104-06542-012	RPD (%)
PBDE-047	61	92	41	61	93	42	91	86	6
PBDE-100	74	116	44	74	116	44	98	93	5
PBDE-099	57	92	47	57	92	47	90	85	6
PBDE-154	53	86	47	53	86	47	88	84	5
PBDE-153	50.00	84	51	50	84	51	84	80	5
PBDE-209	84	116	32	84	116	32	158	172	8

Table B-13. Laboratory Duplicates.

	TJ0701				RPD %	AZ1308				RPD %	TU1404				RPD %
PBDE-047	0.4	U	0.5	U	NA	0.5	U	0.5	U	NA	0.3	U	0.3	U	NA
PBDE-100	0.4	U	0.5	U	NA	0.5	U	0.5	U	NA	0.3	U	0.3	U	NA
PBDE-099	0.4	U	0.5	U	NA	0.5	U	0.5	U	NA	0.3	U	0.3	U	NA
PBDE-154	0.4	U	0.5	U	NA	0.5	U	0.5	U	NA	0.3	U	0.3	U	NA
PBDE-153	0.4	U	0.5	U	NA	0.5	U	0.5	U	NA	0.3	U	0.3	U	NA
PBDE-209	3.3	UJ	3.5	UJ	NA	3.8	U	3.7	U	NA	2.7	UJ	2.7	UJ	NA
	DT0404				RPD %	TR3001				RPD %					
PBDE-047	0.5	U	0.5	U	NA	0.5	U	0.5	U	NA					
PBDE-100	0.5	U	0.5	U	NA	0.5	U	0.5	U	NA					
PBDE-099	0.5	U	0.5	U	NA	0.5	U	0.5	U	NA					
PBDE-154	0.5	U	0.5	U	NA	0.5	UJ	0.5	U	NA					
PBDE-153	0.5	U	0.5	U	NA	0.5	UJ	0.5	U	NA					
PBDE-209	3.7	UJ	3.9	UJ	NA	63	J	50	J	23					

U = undetected at level indicated.
UJ = undetected at level indicated; level is an estimate.
J = report result is an estimate.

Table B-14. Laboratory Matrix Spikes.

	Matrix Spike Recoveries (%)			
	TJ0701	AZ1308	TU1404	DT0404
PBDE-047	56	92	82	71
PBDE-100	62	111	101	82
PBDE-099	60	118	83	72
PBDE-154	69	77	75	73
PBDE-153	64	74	73	72
PBDE-209	36	50	108	162

Appendix C. Initial XRF Screening Concentrations by Product Type

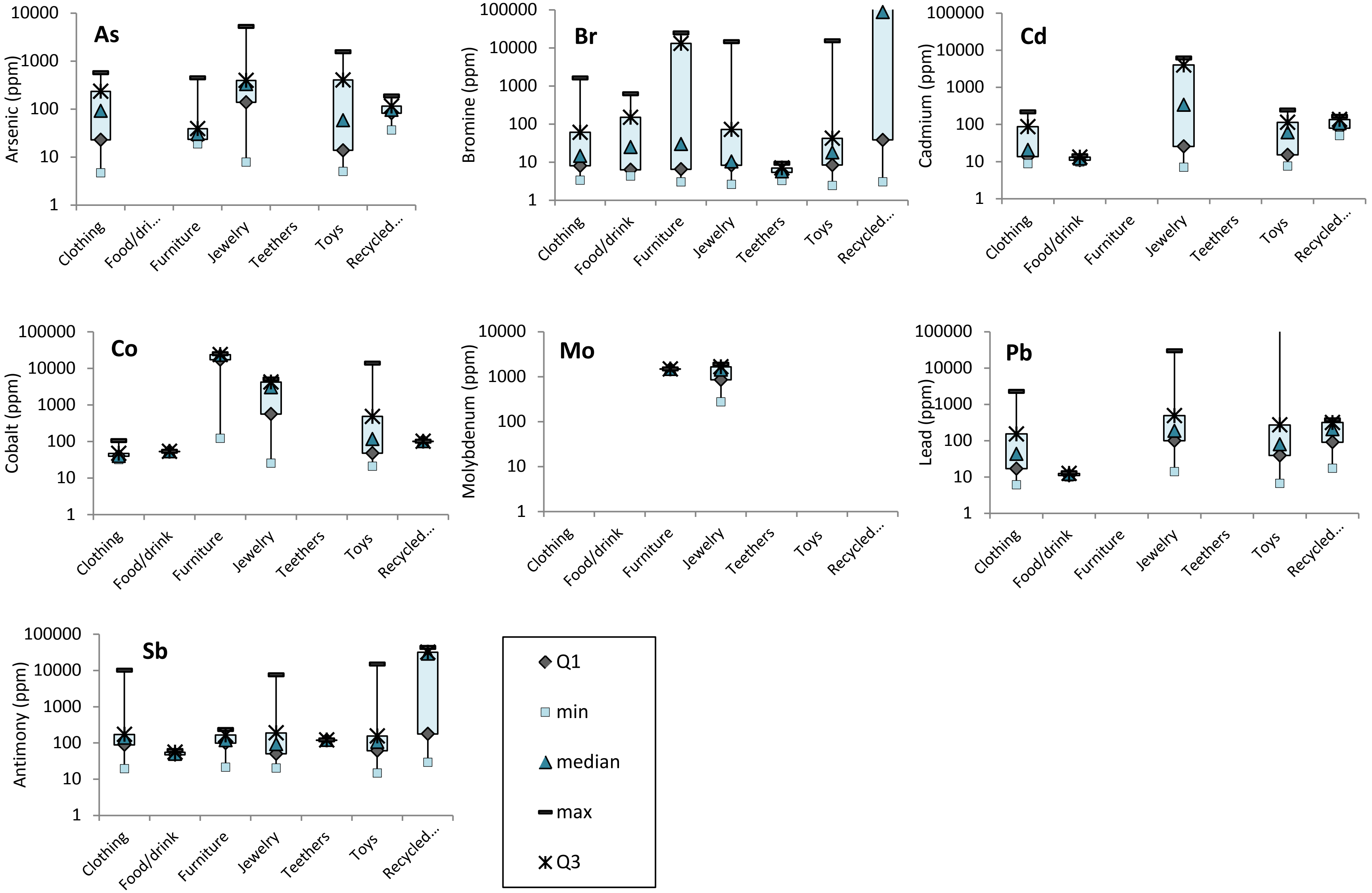

Figure C-2. Boxplots Displaying XRF Initial 30-second Screening Statistics by Product Type for Each Element Analyzed.

Notes for Figure C-2:

(n = 273 (clothing); n = 61 (food/drink); n = 52 (furniture); n = 154 (jewelry); n = 28 (teethers); n = 573 (toys); n = 37 (recycled electronics).

Summary includes only >LOD values. Recycled = recycled electronics. All categories except for “recycled electronics” include products intended for children ages 0-5. “Clothing” includes bedding and linens. “Food/drink” category includes plates, cups, etc. “Teethers” includes pacifiers and other products intended for infants’ mouths. Product selection was not by random selection; summary statistics are not meant to be a representation of products on the market.

Appendix D. Regressions for Laboratory and XRF results

Table D-1. Simple Linear Regression Results for Metal Analytes (non-transformed ppm values).

XRF method	As		Cd		Co		Pb		Sb	
	r^2 (n)	p-value	r^2 (n)	p-value	r^2 (n)	p-value	r^2 (n)	p-value	r^2 (n)	p-value
Initial screening	**1 (14)**	<0.001	**0.99 (20)**	<0.001	0.01 (8)	0.808	**0.91 (26)**	<0.001	**0.51 (34)**	<0.001
60s hand	**0.83 (9)**	0.001	0.01 (10)	0.759	**1 (3)**	0.002	**0.95 (19)**	<0.001	**0.99 (26)**	<0.001
60s stand	**0.99 (10)**	<0.001	**0.99 (10)**	<0.001	**1 (5)**	<0.001	**0.98 (20)**	<0.001	**0.90 (30)**	<0.001
Powder	**1 (6)**	<0.001	**1 (3)**	0.001	0.97 (3)	0.116	**0.99 (10)**	<0.001	**0.81 (8)**	0.002

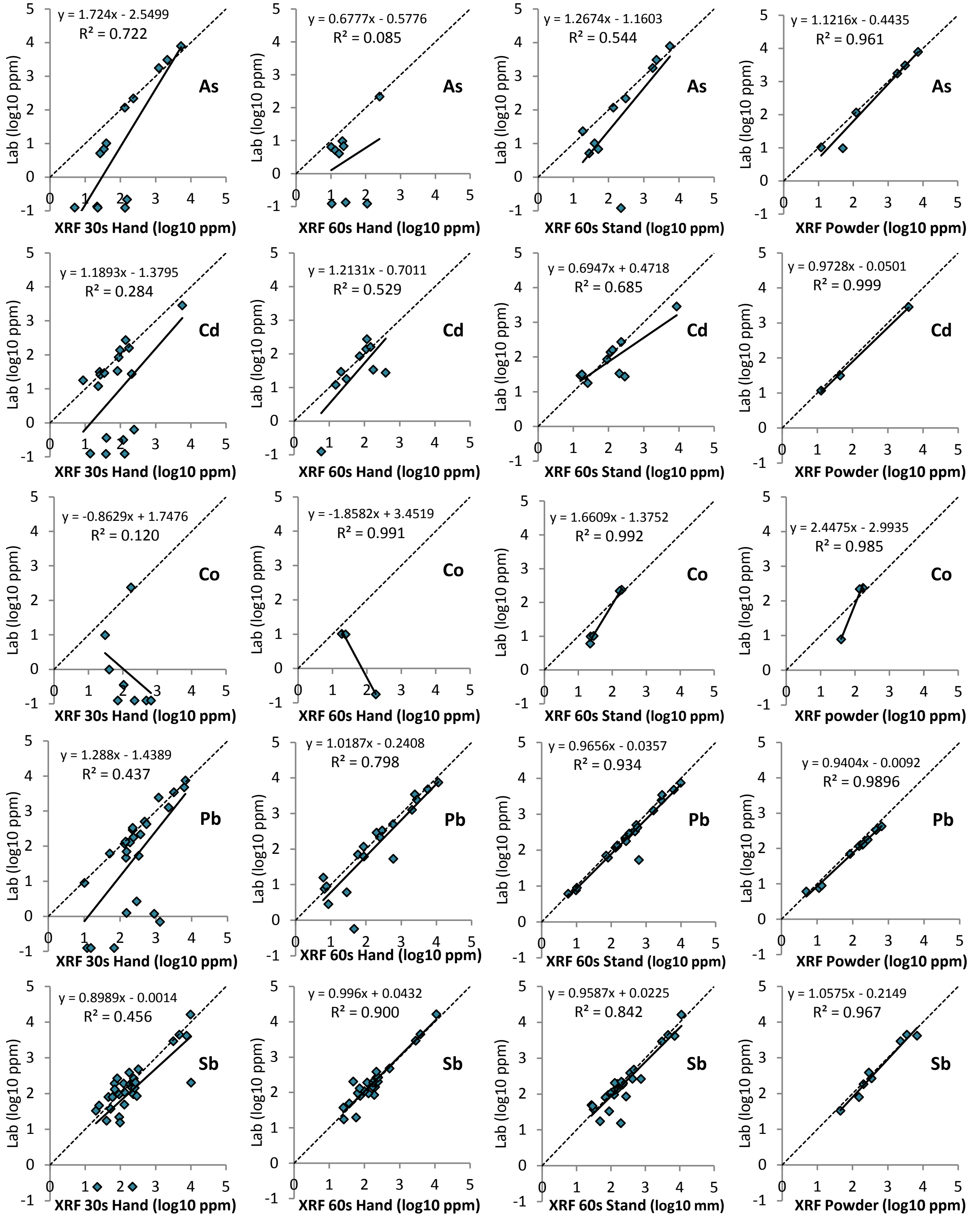

Figure D-1. Linear Regression Plots Between Log$_{10}$ Normalized Values for XRF Screening and Laboratory Results of Metal Analytes. *Dashed line indicates line of equality; solid line indicates regression trendline. XRF 30s Hand = non-isolated material initial screening; XRF 60s Hand, 60s Stand, and Powder = isolated material screening.*

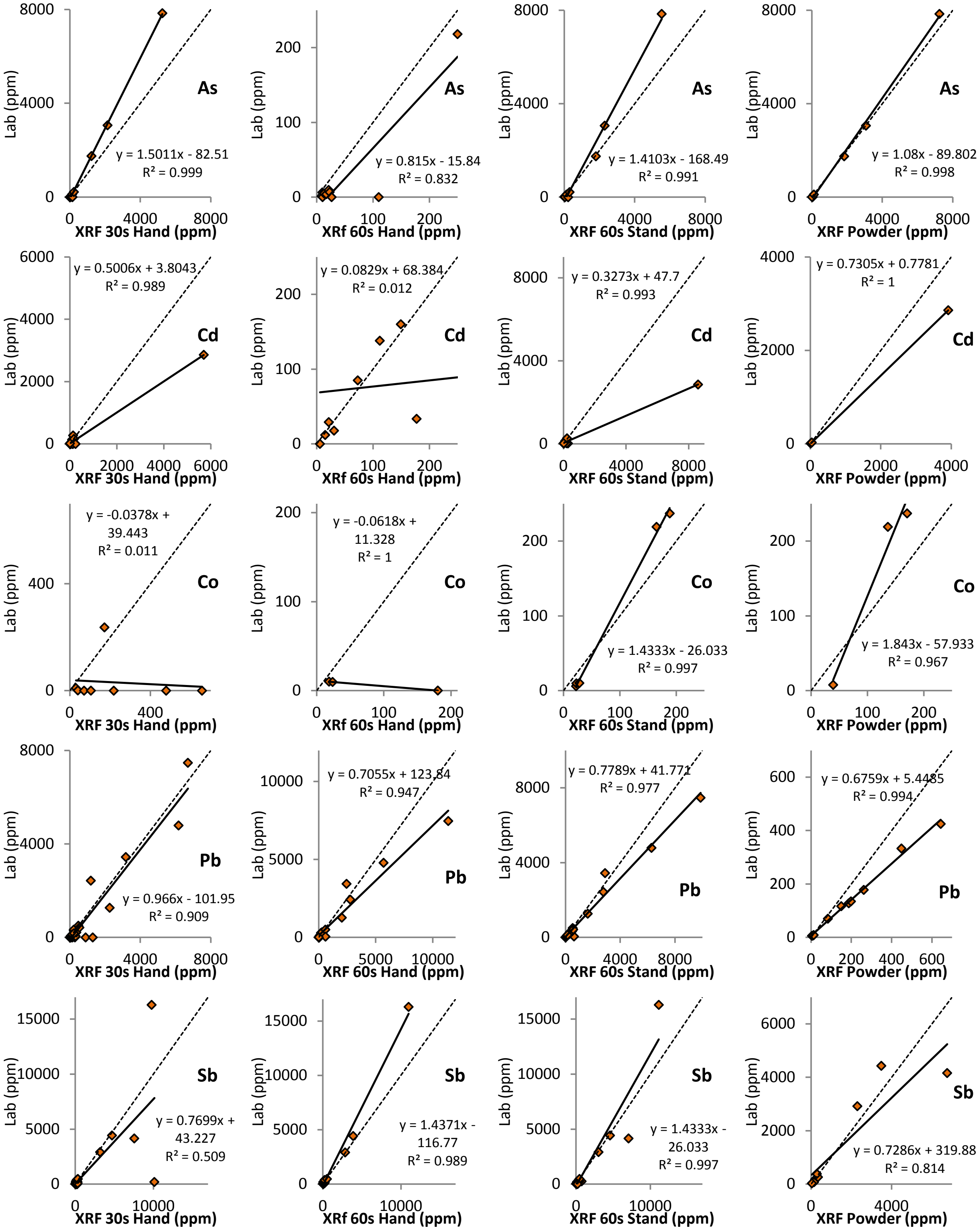

Figure D-2. Linear Regression Plot Between Non-transformed (raw) Values for XRF Screening and Laboratory Results of Metal Analytes. *Dashed line indicates line of equality; solid line indicates regression trendline. XRF 30s Hand = non-isolated material initial screening; XRF 60s Hand, 60s Stand, and Powder = isolated material screening.*

Table D-2. Simple Linear Regression Results for XRF-measured Bromine and Lab PBDE Results (non-transformed ppm values).

XRF method	Br	
	r^2 (n)	p-value
Initial screening	0.03 (23)	0.416
60s hand	0.03 (23)	0.452
60s stand	0.03 (23)	0.407
Powder	0.01 (19)	0.629

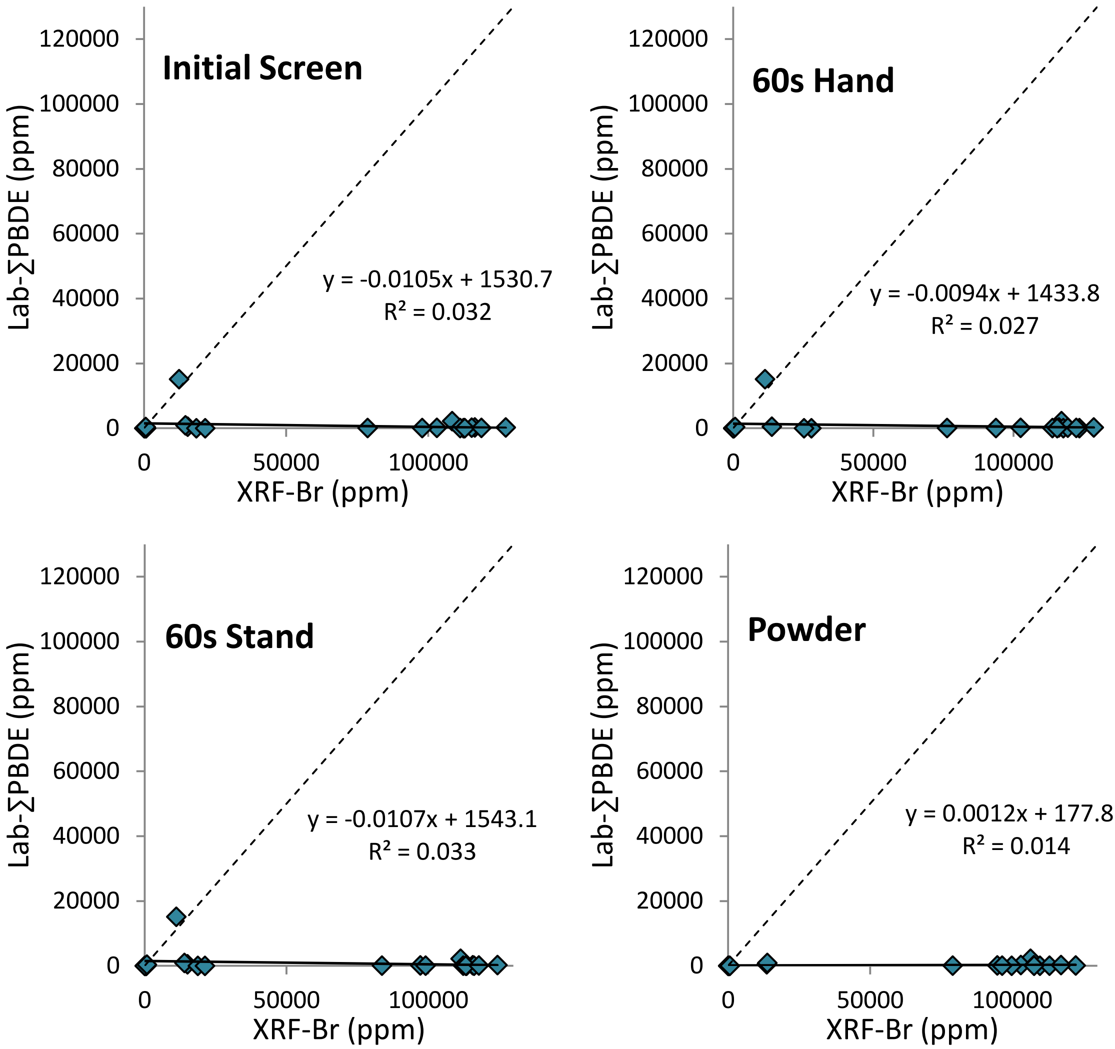

Figure D-3. Linear Regression Plot Between Non-transformed (raw) Values for XRF-measured Bromine and Laboratory PBDE Results.

Dashed line indicates line of equality; solid line indicates regression trendline.

Appendix E. XRF and Laboratory Results for Metal Analytes

Table E-1. Antimony Results for Non-Metals Samples, Method 3052 (all values ppm).

Sample ID	XRF 30s Screen	XRF 60s Hand	XRF 60s Stand	XRF 60s Powder	ICP-MS
AZ0801	22	30 U	26 U	---	0.5 U
AZ0804	69	73	133	---	131
AZ0807	53	25	31	---	37.4
AZ0808	46 U	37 U	34 U	---	0.5 U
AZ1201	51 U	32 U	29 U	32 U	0.5 U
AZ1308	44 U	38 U	31 U	36 U	0.5 U
AZ1604	47 U	33 U	35 U	---	2.2
AZ1702	39 U	39 U	29 U	30 U	0.5 U
AZ1804	221	36 U	34 U	33 U	0.5 U
AZ2007	3,173	2,848	3,023	2,300	2,920
AZ2011	40	26	48	---	17.4
AZ2324	59	---	69	152	79.5
AZ2325	25	---	29	54 U	46.2
AZ2326	20	---	88	45	33
AZ2333	97	---	193	79 U	15.4
AZ2401	46	76	69	---	80.2
BL1301	101 U	63 U	65 U	---	1.6
BL2308	235	194	199	---	220
CL0902	36 U	41 U	53 U	---	0.9 U
DT1601	48 U	---	---	---	15.8
DT2002	54 U	58	40 U	41 U	19.7
DT3001	81	245	420	347	266
DT4202	4,701	3,877	4,569	3,490	4,430
DT4502	178	217	361	290	387
DT6402	39 U	36 U	31 U	32 U	0.5 U
DT6403	37 U	30 U	24 U	---	14.3
DT6404	68	173	153	---	191
DT6701	92	27 U	23 U	---	21.9
DT9404	123	119	184	---	191
TG0901	212	171	---	---	146
TG1001	10,130	241	224	---	202
TG1002	9,780	10,986	11,139	---	16,300 J
TG2301	231	199	210	---	190
TJ0103	32 U	29 U	20 U	---	0.5 U
TJ0104	37 U	25 U	19 U	---	0.5 U
TJ0403	27 U	69 U	68 U	58 U	0.1 U
TJ0701	54 U	45 U	38 U	39 U	0.5 U
TJ0906	292	189	274	---	85.4
TJ1403	49 U	35 U	31 U	33 U	4.1
TJ2402	30 U	34 U	43 U	---	0.5 U
TJ2901	7,555	---	7,065	6,757	4,160 J
TJ3204	189	---	216	204	183
TJ4001	34 U	38 U	32 U	---	1.5
TJ4903	92	130	83	---	94.4
TU0104	46 U	49 U	86 U	---	1.1
TU0203	61 U	58 U	58 U	---	0.76
TU0204	51 U	47 U	107 U	---	0.5 U
TU0301	233	65	123	---	95.8
TU0306	58 U	50 U	81 U	---	9.5
TU0405	131	99	102	---	109
TU0407	246	178	137	---	192
TU0501	240	218	743	---	263
TU0503	129	37	27	---	49.1
TU1404	254	201	157	---	143
TU3102	323	515	461	---	479
WM1004	267	48	128	---	204
WM1501	27 U	83 U	64 U	63 U	0.1 U

U = undetected at level indicated.
J = report result is an estimate.

Table E-2. Arsenic Results for Non-Metals Samples, Method 3052 (all values ppm).

Sample ID	XRF 30s Screen	XRF 60s Hand	XRF 60s Stand	XRF 60s Powder	ICP-MS
AZ0801	104 U	134 U	133 U	---	0.2 U
AZ0804	31 U	5 U	5 U	---	0.2 U
AZ0807	202 U	200 U	206 U	---	1.3
AZ0808	5 U	4 U	3 U	---	0.2 U
AZ1201	10 U	3 U	3 U	4 U	0.3 J
AZ1308	13 U	4 U	3 U	4 U	0.3 U
AZ1604	22	27	26 U	---	0.3 U
AZ1702	7 U	4 U	3 U	3 U	0.2 U
AZ1804	7 U	4 U	4 U	4 U	0.2 U
AZ2007	20 U	18 U	15 U	13 U	1.1 J
AZ2011	51 U	26 U	43 U	---	1
AZ2324	2,142	---	2,297	3,074	3,060
AZ2325	5,250	---	5,530	7,243	7,840
AZ2326	1,231	---	1,799	1,838	1,750
AZ2333	133	---	137	121	116
AZ2401	61 U	60 U	61 U	---	1.5
BL1301	15 U	10 U	19 U	---	0.5
BL2308	5 U	4 U	5 U	---	0.3 J
CL0902	154	4 U	8 U	---	0.4 U
DT1601	26 U	---	---	---	1.2 J
DT2002	35 U	17 U	21 U	25 U	4.4
DT3001	26 U	10	12 U	13 U	6.4
DT4202	17 U	16 U	15 U	12	10.3
DT4502	27 U	21	29 U	50	9.7
DT6402	6 U	3 U	3 U	3 U	0.2 U
DT6403	30 U	27 U	25 U	---	0.7
DT6404	80 U	4 U	7 U	---	0.2 U
DT6701	15 U	11	11 U	---	0.2 U
DT9404	5	4 U	7 U	---	0.2 U
TG0901	11 U	4 U	---	---	0.2 U
TG1001	6	4 U	6 U	---	0.1 U
TG1002	21 U	17	17 U	---	4.1
TG2301	11 U	4 U	9 U	---	0.1 U
TJ0103	52 U	58 U	56 U	---	0.2 U
TJ0104	54 U	12 U	11 U	---	0.2 U
TJ0403	10 U	6 U	7 U	7 U	2.6
TJ0701	8 U	6 U	6 U	6 U	0.2 U
TJ0906	18 U	13 U	13 U	---	0.2
TJ1403	7 U	4 U	5 U	5 U	0.2 U
TJ2402	135	110	226	---	0.2 U
TJ2901	35 U	---	19	25 U	23.1
TJ3204	9 U	---	5 U	5 U	1.2 J
TJ4001	8 U	4 U	4 U	---	0.2 U
TJ4903	210 U	304 U	202 U	---	1.2 J
TU0104	40	15 U	40	---	10.1
TU0203	23	7 U	8 U	---	0.2 U
TU0204	34	23	51	---	6.8
TU0301	5 U	4 U	7 U	---	0.1 U
TU0306	27	13	28	---	5.1
TU0405	6 U	4 U	11 U	---	0.2 U
TU0407	5 U	4 U	7 U	---	0.1 U
TU0501	93 U	64 U	76 U	---	0.8 J
TU0503	60 U	7 U	10 U	---	0.2 U
TU1404	6 U	4 U	6 U	---	0.1
TU3102	233	250	306	---	218
WM1004	15 U	5 U	23 U	---	0.1 U
WM1501	11 U	8 U	6 U	7 U	0.7

U = undetected at level indicated.

J = report result is an estimate.

Table E-3. Cadmium Results for Non-Metals Samples, Method 3052 (all values ppm).

Sample ID	XRF 30s Screen	XRF 60s Hand	XRF 60s Stand	XRF 60s Powder	ICP-MS
AZ0801	39	17 U	15 U	---	0.2 U
AZ0804	132	19 U	18 U	---	0.2 U
AZ0807	35	22	16	---	29.2
AZ0808	21 U	17 U	15 U	---	0.2 U
AZ1201	23 U	15 U	13 U	15 U	0.2 U
AZ1308	19 U	17 U	14 U	16 U	0.3 U
AZ1604	21 U	15 U	16 U	---	0.3 U
AZ1702	18 U	17 U	13 U	14 U	0.2 U
AZ1804	22 U	16 U	15 U	15 U	0.2 U
AZ2007	24 U	20 U	17 U	14 U	0.2 U
AZ2011	89	73	91	---	85.0
AZ2324	26	---	18	44	31.6
AZ2325	12 U	---	10 U	25 U	7.3 J
AZ2326	12 U	---	38 U	26 U	2.6
AZ2333	5,700	---	8,592	3,914	2,860
AZ2401	97	112	114	---	138
BL1301	141	117	229	---	272
BL2308	23 U	17 U	17 U	---	0.1 U
CL0902	20 U	18 U	24 U	---	0.43 U
DT1601	22 U	---	---	---	3.2
DT2002	26 U	24 U	19 U	19 U	3.4
DT3001	26 U	18 U	17 U	13	11.7
DT4202	28 U	26 U	23 U	21 U	0.55
DT4502	25 U	18 U	15 U	16 U	6.5
DT6402	40	16 U	14 U	14 U	0.36
DT6403	176	149	131	---	160
DT6404	120	18 U	23 U	---	0.31
DT6701	83	177	203	---	33.6
DT9404	24 U	17 U	24 U	---	0.2 U
TG0901	34 U	18 U	---	---	0.2 U
TG1001	27 U	17 U	21 U	---	0.1 U
TG1002	22 U	20 U	15 U	---	0.1 U
TG2301	35 U	18 U	30 U	---	0.16
TJ0103	209	399	290	---	27.4
TJ0104	244	14 U	11 U	---	0.63
TJ0403	14	30 U	30 U	26 U	0.07 J
TJ0701	24 U	21 U	17 U	18 U	0.2 U
TJ0906	22 U	18 U	15 U	---	0.41
TJ1403	22 U	16 U	14 U	15 U	0.2 U
TJ2402	14 U	16 U	21 U	---	0.2 U
TJ2901	27	---	30 U	28 U	26.0
TJ3204	24 U	---	16 U	15 U	1.2
TJ4001	18 U	17 U	15 U	---	0.2 U
TJ4903	17 U	31	26	---	17.8
TU0104	24 U	25 U	44 U	---	0.2 U
TU0203	28 U	26 U	26 U	---	0.2 U
TU0204	25 U	24 U	51 U	---	0.2 U
TU0301	23 U	19 U	21 U	---	0.1 U
TU0306	29 U	26 U	43 U	---	0.2 U
TU0405	22 U	17 U	29 U	---	0.2 U
TU0407	23 U	18 U	22 U	---	0.1 U
TU0501	23	15	34 U	---	12.0
TU0503	14	6	11 U	---	0.2 U
TU1404	23 U	17 U	22 U	---	0.1 U
TU3102	32 U	18 U	19 U	---	4.9
WM1004	48 U	24 U	65 U	---	0.1 U
WM1501	10	36 U	28 U	29 U	0.04 J

U = undetected at level indicated.
J = report result is an estimate.

Table E-4. Cobalt Results for Non-Metals Samples, Method 3052 (all values ppm).

Sample ID	XRF 30s Screen	XRF 60s Hand	XRF 60s Stand	XRF 60s Powder	ICP-MS
AZ0801	91 U	101 U	89 U	---	0.24 U
AZ0804	70 U	23 U	27 U	---	0.55
AZ0807	114 U	106 U	89 U	---	0.37
AZ0808	36 U	27 U	27 U	---	0.25 U
AZ1201	47 U	20 U	20 U	21 U	0.25 U
AZ1308	27 U	21 U	17 U	22 U	0.25 U
AZ1604	32 U	25 U	29 U	---	0.27 U
AZ1702	478	25 U	19 U	20 U	0.25 U
AZ1804	31 U	23 U	22 U	20 U	0.25 U
AZ2007	155 U	121 U	101 U	86 U	0.25 U
AZ2011	177 U	104 U	103 U	---	0.62
AZ2324	251 U	---	165	136	219.0
AZ2325	172	---	188	170	237.0
AZ2326	180 U	---	115 U	76 U	4.5
AZ2333	53 U	---	65 U	37 U	0.33
AZ2401	108 U	107 U	96 U	---	1.2
BL1301	66 U	41 U	50 U	---	0.56
BL2308	33 U	23 U	22	---	6.1
CL0902	29 U	21 U	37 U	---	0.43 U
DT1601	67 U	---	---	---	127.0
DT2002	105 U	55 U	59 U	66 U	1.3
DT3001	63 U	38 U	34 U	37 U	4.8
DT4202	30	24	23	30 U	9.8
DT4502	45 U	35 U	36 U	49 U	2.5
DT6402	24 U	20 U	17 U	19 U	0.25 U
DT6403	142 U	102 U	93 U	---	0.55
DT6404	170 U	24 U	41 U	---	1.4
DT6701	100 U	83 U	78 U	---	0.24 U
DT9404	218	22 U	40 U	---	0.25 U
TG0901	71 U	23 U	---	---	0.24 U
TG1001	40	21 U	29 U	---	1.0
TG1002	105	180	81 U	---	0.35
TG2301	66 U	23 U	50 U	---	0.1 U
TJ0103	109 U	90 U	58 U	---	0.25 U
TJ0104	124 U	84 U	63 U	---	0.25 U
TJ0403	112 U	39 U	40 U	38 U	0.2 U
TJ0701	34 U	28 U	24 U	24 U	0.25 U
TJ0906	130 U	101 U	92 U	---	0.10 U
TJ1403	71	19 U	18 U	21 U	0.25 U
TJ2402	22 U	23 U	42 U	---	0.24 U
TJ2901	65 U	---	48 U	39	7.8
TJ3204	35 U	---	22 U	21 U	1.5
TJ4001	656	23 U	22 U	---	0.25 U
TJ4903	176 U	141 U	141 U	---	1.4
TU0104	27 U	23 U	55 U	---	0.24 U
TU0203	34 U	31 U	36 U	---	0.25 U
TU0204	26 U	20 U	70 U	---	0.24 U
TU0301	33 U	25 U	31 U	---	0.10 U
TU0306	28 U	24 U	52 U	---	0.25 U
TU0405	28 U	22 U	50 U	---	0.25 U
TU0407	29 U	23 U	37 U	---	0.12
TU0501	149 U	103 U	60 U	---	0.40
TU0503	130 U	96 U	63 U	---	0.25 U
TU1404	34 U	19	28	---	10.2
TU3102	48 U	23 U	27 U	---	0.25 U
WM1004	89 U	31 U	158 U	---	8.4
WM1501	106 U	48 U	38 U	39 U	0.1 U

U = undetected at level indicated.

Table E-5. Lead Results for Non-Metals Samples, Method 3052 (all values ppm).

Sample ID	XRF 30s Screen	XRF 60s Hand	XRF 60s Stand	XRF 60s Powder	ICP-MS
AZ0801	1,193	2,772	2,773	---	2430
AZ0804	152	6 U	7 U	---	1.3
AZ0807	6,169	5,691	6,285	---	4790
AZ0808	6 U	5 U	4 U	---	0.9
AZ1201	12	4 U	4 U	5 U	0.25 U
AZ1308	68	5 U	4 U	4 U	0.25 U
AZ1604	225	200	328	---	290
AZ1702	8 U	5 U	4 U	4 U	0.46
AZ1804	11 U	4 U	5 U	5 U	0.25 U
AZ2007	21 U	19 U	15 U	13 U	3.2
AZ2011	372	247	252	---	217
AZ2324	143	---	149	198	135
AZ2325	547	---	564	644	425
AZ2326	238	---	266	262	178
AZ2333	25 U	---	45 U	37 U	17.5
AZ2401	485	586	524	---	502
BL1301	18 U	12 U	25 U	---	15.8
BL2308	7 U	5 U	6 U	---	0.71 J
CL0902	26 U	5 U	10 U	---	1.1
DT1601	147	---	---	---	46.8
DT2002	134	85	132	150	117
DT3001	152	59	71	84	70.2
DT4202	40 U	28	36 U	32 U	6.1
DT4502	226	289	480	449	333
DT6402	15	4 U	4 U	4 U	0.25 U
DT6403	52	88	81	---	61.7
DT6404	1,302	6 U	8 U	---	0.7
DT6701	17 U	11 U	12 U	---	0.73
DT9404	8 U	5 U	9 U	---	0.36
TG0901	13 U	6 U	---	---	1.2
TG1001	9 U	5 U	7 U	---	0.41 J
TG1002	24 U	19 U	20 U	---	0.1 U
TG2301	12 U	5 U	10 U	---	1.2 J
TJ0103	332	596	621	---	53.2
TJ0104	291	13 U	14 U	---	2.7
TJ0403	13 U	8 U	9 U	9 U	0.4 J
TJ0701	10	8	10	13	9
TJ0906	18 U	14 U	12 U	---	0.21
TJ1403	9 U	7	10	11	7.6
TJ2402	3,177	2,444	2,891	---	3440
TJ2901	190	---	146	187	128
TJ3204	12 U	---	6	5	6.1
TJ4001	9 U	4 U	5 U	---	0.39
TJ4903	6,699	11,364	9,872	---	7470
TU0104	42 U	46	61 U	---	0.57
TU0203	36 U	9 U	11 U	---	4
TU0204	38 U	46 U	70 U	---	0.61
TU0301	6 U	5 U	8 U	---	0.25 J
TU0306	46 U	48 U	64 U	---	0.93
TU0405	8 U	6 U	15 U	---	0.32
TU0407	6 U	5 U	9 U	---	0.45 J
TU0501	2,262	2,029	1,624	---	1270
TU0503	898	9 U	10 U	---	1.2
TU1404	7 U	5 U	8 U	---	0.34 J
TU3102	16 U	9	10 U	---	2.8
WM1004	18 U	7 U	22 U	---	0.42 J
WM1501	13 U	9 U	8 U	9 U	0.1 U

U = undetected at level indicated.
J = report result is an estimate.

Table E-6. Mercury Results for Non-Metals Samples, Method 3052 (all values ppm).

Sample ID	XRF 30s Screen	XRF 60s Hand	XRF 60s Stand	XRF 60s Powder	ICP-MS
AZ0801	38 U	39 U	37 U	---	0.005 U
AZ0804	24 U	9 U	14 U	---	0.005 U
AZ0807	45 U	45 U	42 U	---	0.017
AZ0808	11 U	8 U	8 U	---	0.005 U
AZ1201	18 U	8 U	10 U	10 U	0.006 U
AZ1308	11 U	8 U	7 U	10 U	0.013 U
AZ1604	12 U	9 U	11 U	---	0.019 U
AZ1702	18 U	9 U	7 U	8 U	0.005 U
AZ1804	16 U	10 U	11 U	9 U	0.005 U
AZ2007	54 U	45 U	37 U	34 U	0.005 U
AZ2011	58 U	37 U	37 U	---	0.014
AZ2324	45 U	---	38 U	33 U	0.005 U
AZ2325	51 U	---	43 U	32 U	0.010 U
AZ2326	39 U	---	36 U	27 U	0.010 U
AZ2333	62 U	---	94 U	81 U	0.010 U
AZ2401	39 U	33 U	35 U	---	0.011
BL1301	40 U	25 U	44 U	---	0.005 U
BL2308	12 U	8 U	14 U	---	0.007 U
CL0902	602	9 U	25 U	---	0.041 U
DT1601	18 U	---	---	---	0.073 U
DT2002	30 U	15 U	18 U	19 U	0.123
DT3001	18 U	11 U	10 U	11 U	0.057
DT4202	21 U	18 U	18 U	17 U	0.005 U
DT4502	14 U	11 U	12 U	15 U	0.090
DT6402	9 U	8 U	7 U	8 U	0.005 U
DT6403	45 U	35 U	34 U	---	0.005
DT6404	44 U	9 U	22 U	---	0.005 U
DT6701	37 U	28 U	27 U	---	0.008 U
DT9404	18 U	9 U	24 U	---	0.011 U

Sample ID	XRF 30s Screen	XRF 60s Hand	XRF 60s Stand	XRF 60s Powder	ICP-MS
TG0901	33 U	9 U	---	---	0.005 U
TG1001	17 U	8 U	16 U	---	0.005 U
TG1002	39 U	36 U	32 U	---	0.015 U
TG2301	28 U	10 U	32 U	---	0.005 U
TJ0103	35 U	30 U	28 U	---	0.005 U
TJ0104	40 U	28 U	34 U	---	0.005 U
TJ0403	34 U	14 U	15 U	19 U	0.019 U
TJ0701	15 U	12 U	11 U	12 U	0.005 U
TJ0906	48 U	34 U	37 U	---	0.026 U
TJ1403	14 U	7 U	8 U	9 U	0.006 U
TJ2402	14 U	14 U	27 U	---	0.010 U
TJ2901	31 U	---	22 U	21 U	0.134
TJ3204	14 U	---	8 U	8 U	0.005 U
TJ4001	18 U	9 U	11 U	---	0.014
TJ4903	69 U	55 U	53 U	---	0.005 U
TU0104	29 U	21 U	67 U	---	0.007 UJ
TU0203	34 U	14 U	22 U	---	0.025
TU0204	31 U	22 U	87 U	---	0.005 UJ
TU0301	13 U	10 U	18 U	---	0.006 U
TU0306	31 U	24 U	63 U	---	0.005 UJ
TU0405	11 U	9 U	35 U	---	0.022 U
TU0407	11 U	9 U	23 U	---	0.005 U
TU0501	35 U	27 U	22 U	---	0.015
TU0503	38 U	22 U	27 U	---	0.005 UJ
TU1404	13 U	9 U	16 U	---	0.005 U
TU3102	22 U	10 U	15 U	---	0.015
WM1004	49 U	11 U	103 U	---	0.005 U
WM1501	37 U	17 U	14 U	19 U	0.017 U

U = undetected at level indicated.
UJ = undetected at the level indicated; level is an estimate.

Table E-7. Molybdenum Results for Non-Metals Samples, Method 3052 (all values ppm).

Sample ID	XRF 30s Screen	XRF 60s Hand	XRF 60s Stand	XRF 60s Powder	ICP-MS
AZ0801	---	---	---	---	191.0
AZ0804	---	---	---	---	33.9
AZ0807	---	---	---	---	0.2 U
AZ0808	---	---	---	---	3.1 J
AZ1201	---	---	---	---	0.2 U
AZ1308	---	---	---	---	0.3 U
AZ1604	---	---	---	---	0.66 J
AZ1702	---	---	---	---	0.2 U
AZ1804	---	---	---	---	0.2 U
AZ2007	---	---	---	---	0.4 U
AZ2011	399 U	167 U	---	---	0.35
AZ2324	46 U	---	62 U	---	0.3 U
AZ2325	43 U	---	35 U	---	0.2 U
AZ2326	49 U	---	---	---	0.2 U
AZ2333	---	---	---	---	0.2 U
AZ2401	---	---	---	---	1.4
BL1301	---	---	---	---	0.4 J
BL2308	---	---	---	---	0.1 U
CL0902	---	---	---	---	0.4 U
DT1601	---	---	---	---	1.0 U
DT2002	---	---	---	---	2.6
DT3001	---	---	---	---	1.5
DT4202	---	---	---	---	0.2 U
DT4502	---	---	---	---	1.9
DT6402	---	---	---	---	0.2 U
DT6403	---	---	---	---	0.2 U
DT6404	363 U	---	---	---	0.2 U
DT6701	---	---	---	---	0.2 U
DT9404	---	---	---	---	0.2 U
TG0901	---	---	---	---	0.2 U
TG1001	---	---	---	---	0.1 U
TG1002	---	---	---	---	0.1 U
TG2301	---	---	---	---	0.1 U
TJ0103	---	---	---	---	0.2 U
TJ0104	---	---	---	---	0.2 U
TJ0403	245 U	---	---	---	0.5 U
TJ0701	---	---	---	---	0.2 U
TJ0906	---	---	---	---	0.1 U
TJ1403	---	---	---	---	0.2 U
TJ2402	---	---	---	---	0.2 U
TJ2901	---	---	---	---	2.8
TJ3204	---	---	---	---	0.2 U
TJ4001	---	---	---	---	0.2 U
TJ4903	60 U	---	253 U	---	0.2 U
TU0104	---	---	---	---	0.2 U
TU0203	---	---	---	---	0.2 U
TU0204	---	---	---	---	0.2 U
TU0301	---	---	---	---	0.1 U
TU0306	---	---	---	---	0.2 U
TU0405	---	---	---	---	0.1 U
TU0407	---	---	---	---	0.2 U
TU0501	213 U	169 U	---	---	0.2 U
TU0503	160 U	124 U	---	---	0.7 J
TU1404	---	---	---	---	0.1 U
TU3102	---	---	---	---	0.2 U
WM1004	---	---	---	---	0.1 U
WM1501	219 U	---	---	---	0.5 U

U = undetected at level indicated.
J = report result is an estimate.

Table E-8. Antimony Results for Metal Samples, Method 3050B (all values ppm).

Sample ID	XRF 30s Screen	XRF 60s Hand	XRF 60s Stand	XRF 60s Powder	ICP-MS
AZ0503	236 U	162 U	151 U	---	0.5 J
AZ0504	14,972	9,260	3,265	---	5,470
AZ1605	109 U	85 U	82 U	---	2.1
AZ2013	147 U	78 U	149 U	---	0.2 U
BL2408	156 U	43 U	90 U	---	0.6 J
CL0201	208 U	42 U	187 U	---	2.6
CL1601	163 U	110 U	111 U	---	1.8
TJ4701	192 U	131 U	144 U	---	0.2 UJ
TJ4801	6,820	2,558	6,769	---	1,640
TJ4902	169 U	41 U	136 U	---	0.2 U
TU1302	42 U	46 U	139 U	---	0.6 J
TU2307	132 U	98 U	110 U	---	8.9
TU2406	70 U	144 U	132 U	---	0.2 U
WM0601	118	61 U	80	---	42.2
WM0606	106 U	33 U	105 U	---	2.0 U

U = undetected at level indicated.
UJ = undetected at the level indicated; level is an estimate.
J = report result is an estimate.

Table E-9. Arsenic Results for Metal Samples, Method 3050B (all values ppm).

Sample ID	XRF 30s Screen	XRF 60s Hand	XRF 60s Stand	XRF 60s Powder	ICP-MS
AZ0503	602	421 U	408 U	---	17.6
AZ0504	2990 U	1,368 U	603 U	---	115
AZ1605	86 U	66 U	46	---	62.8
AZ2013	1,561	1,059	1,317	---	19.8
BL2408	109 U	23 U	66 U	---	20.9
CL0201	151 U	21	152 U	---	26.4
CL1601	104 U	66 U	76 U	---	15.3
TJ4701	157 U	102 U	105 U	---	17
TJ4801	1,639 U	593 U	1,265 U	---	8.7 J
TJ4902	1,497	292	1,559	---	17
TU1302	572	354	194 U	---	6.5
TU2307	114 U	83 U	79 U	---	91.5
TU2406	1,392	1,283	1,267	---	17
WM0601	159	52	149	---	236
WM0606	447	25 U	167 U	---	12.7

U = undetected at level indicated.
J = report result is an estimate.

Table E-10. Cadmium Results for Metal Samples, Method 3050B (all values ppm).

Sample ID	XRF 30s Screen	XRF 60s Hand	XRF 60s Stand	XRF 60s Powder	ICP-MS
AZ0503	110 U	79 U	59	---	22.1
AZ0504	95 U	69 U	28 U	---	13.8
AZ1605	44 U	35 U	35 U	---	0.1 U
AZ2013	63 U	33 U	61 U	---	7.4
BL2408	67 U	23 U	39 U	---	0.1 U
CL0201	85 U	22 U	91 U	---	0.1 U
CL1601	65 U	43 U	48 U	---	0.1 U
TJ4701	85 U	55 U	67 U	---	7.3
TJ4801	3,759	1,701	3,544	---	4,830
TJ4902	86 U	22 U	66 U	---	13.4
TU1302	26 U	26 U	62 U	---	1.4
TU2307	61 U	39 U	49 U	---	0.11
TU2406	44 U	61 U	57 U	---	0.41
WM0601	46 U	26 U	40 U	---	0.9 U
WM0606	41 U	18 U	44 U	---	1.0 U

U = undetected at level indicated.

Table E-11. Cobalt Results for Metal Samples, Method 3050B (all values ppm).

Sample ID	XRF 30s Screen	XRF 60s Hand	XRF 60s Stand	XRF 60s Powder	ICP-MS
AZ0503	295 U	231 U	223 U	---	0.27
AZ0504	387 U	226 U	40	---	0.9 U
AZ1605	2,709	1,414	1,587	---	61.4
AZ2013	277 U	161 U	245 U	---	0.14
BL2408	24,921	3,339	17,797	---	74.8
CL0201	2,538	238	1,697	---	43.3
CL1601	4,303	4,027	4,437	---	11.1
TJ4701	414 U	200 U	196 U	---	0.1 U
TJ4801	1,693 U	631 U	1,296 U	---	10.9
TJ4902	256 U	29 U	220 U	---	0.10
TU1302	132 U	40	217 U	---	0.38
TU2307	3,031	2,774	3,240	---	46.0
TU2406	189	218 U	203 U	---	0.1 U
WM0601	23,285	8,137	22,785	---	106.0
WM0606	2,309 U	573	4,679	---	30.8

U = undetected at level indicated.

Table E-12. Lead Results for Metal Samples, Method 3050B (all values ppm).

Sample ID	XRF 30s Screen	XRF 60s Hand	XRF 60s Stand	XRF 60s Powder	ICP-MS
AZ0503	445	345	307	---	84.4
AZ0504	203,095	64,379	40,240	---	90800
AZ1605	91 U	59	32 U	---	0.7 J
AZ2013	4,096	3,777	12,365	---	289
BL2408	133 U	19	83 U	---	0.2 J
CL0201	213 U	19 U	184 U	---	2.5 J
CL1601	99	90 U	98 U	---	0.9 J
TJ4701	188 U	130 U	113 U	---	74.5
TJ4801	29,704	16,035	28,093	---	27900
TJ4902	2,568	60 U	2,456	---	137
TU1302	80 U	58 U	114	---	18.3
TU2307	128	97	174	---	3.4
TU2406	283 U	1,106	1,505	---	32.5
WM0601	102 U	44 U	88 U	---	1.0 J
WM0606	51 U	29 U	73 U	---	1.4 J

U = undetected at level indicated.
J = report result is an estimate.

Table E-13. Mercury Results for Metal Samples, Method 3050B (all values ppm).

Sample ID	XRF 30s Screen	XRF 60s Hand	XRF 60s Stand	XRF 60s Powder	ICP-MS
AZ0503	2,690 U	2,176 U	2,092 U	---	0.006 U
AZ0504	810 U	614 U	125 U	---	0.083
AZ1605	236 U	189 U	178 U	---	0.005 U
AZ2013	1,107 U	537 U	1,925 U	---	0.006
BL2408	378 U	61 U	222 U	---	0.006 U
CL0201	532 U	62 U	699 U	---	0.005 U
CL1601	313 U	229 U	258 U	---	0.005 U
TJ4701	760	387	522	---	0.021
TJ4801	537 U	241 U	487 U	---	0.005 UJ
TJ4902	988 U	1,197	814 U	---	0.037
TU1302	3,184	1,582	925 U	---	0.052
TU2307	330 U	211 U	268 U	---	0.005 U
TU2406	6,884	509 U	527 U	---	0.005 U
WM0601	300 U	149 U	305 U	---	0.005 U
WM0606	549 U	202	893 U	---	0.005 U

U = undetected at level indicated.
UJ = undetected at the level indicated; level is an estimate.

Table E-14. Molybdenum Results for Metal Samples, Method 3050B (all values ppm).

Sample ID	XRF 30s Screen	XRF 60s Hand	XRF 60s Stand	XRF 60s Powder	ICP-MS
AZ0503	533 U	328 U	299 U	---	0.5 U
AZ0504	588 U	813 U	---	---	4.7 U
AZ1605	237 U	177 U	165 U	---	41.8
AZ2013	410 U	501 U	297 U	---	0.2 U
BL2408	1,480	---	984 U	---	4.9 U
CL0201	386 U	---	826 U	---	7.6
CL1601	302 U	227 U	238 U	---	5.1 J
TJ4701	693 U	276 U	358 U	---	0.5 U
TJ4801	358 U	143 U	283 U	---	484.0 U
TJ4902	863 U	---	715 U	---	0.5 U
TU1302	---	---	348 U	---	0.5 U
TU2307	280 U	204 U	215 U	---	35.8
TU2406	---	294 U	606 U	---	0.5 U
WM0601	2,085 U	903 U	1,773 U	---	41.1
WM0606	206 U	---	216 U	---	9.1

U = undetected at level indicated.
J = report result is an estimate.

Appendix F. XRF and Laboratory Results for Bromine and PBDEs

Table F-1. Results of XRF-measured bromine and lab-measured PBDEs (all values ppm).

Sample ID	XRF 30s Screen Br	XRF 60s Hand Br	XRF 60s Stand Br	XRF 60s Powder Br	Lab PBDEs
AZ0504	2,012	680	943	---	1.6 UJ
AZ1205	270	204	286	272	17 NJ
AZ1305	11	3.1	4 U	3 U	4 U
AZ1308	3.8	3.8	3 U	4 U	3.8 U
AZ1404	4 U	3 U	3 U	3.8	3.6 UJ
AZ1804	673	3.1	4 U	3 U	0.6 NJ
BL0201	4 U	5.9	4 U	10	3.5 NJ
BL0303	293	5.0	5 U	457	13 NJ
BL1402	1,985	4 U	5 U	35	3.6 U
BL1408	359	713	1,030	4 U	3.2 U
BL2101	592	222	441	---	3.1 UJ
CL0101	1,304	968	15	---	6.2 U
DT0404	331	320	402	---	3.7 UJ
DT0507	3.4	5.9	3 U	4 U	3.9 U
DT2503	4 U	3.4	2.3	2.2	7 J
DT3001	235	629	736	788	35 UJ
DT3501	590	517	782	---	3.4 UJ
DT4202	15,312	13,770	15,076	13,568	492.7 J
DT4401	2,746	14	19	20	3.3 UJ
DT5201	3.5	4.2	3 U	3 U	4 U
DT6701	32	9 U	8 U	---	2 UJ
DT9204	592	596	674	---	2.5 UJ
FM0101	12,279	11,331	11,132	---	15140 J
TG0206	2,161	5.0	4 U	3 U	3.8 U
TG0901	115	198	---	---	2.7 UJ
TG1001	11	6.3	6 U	---	2.1 UJ
TG1002	27	35	30	---	300 U
TG2301	11 U	5.5	12 U	---	2.5 UJ
TJ0202	2.6	2.5	3 U	14 U	5.5 U
TJ0403	5 U	5 U	6 U	7 U	3.9 U
TJ0701	6.8	6.4	7.0	4.7	3.3 UJ
TJ0801	20	13	23	29	3.9 UJ
TJ1403	6 U	4.0	2.2	3.6	3.8 U
TJ2001	14 U	13 U	9 U	8.7	2.2 UJ
TJ2301	7 U	3.5	5 U	3 U	3.6 UJ
TJ2901	14,523	---	14,000	13,770	902.4 J
TJ3204	550	---	562	575	10 NJ
TR0201	103,039	102,576	97,173	94,737	136.4 J
TR0401	108,413	117,162	111,359	106,435	2200 J
TR0501	116,401	116,252	113,457	103,031	260 J
TR0601	96,246	106,090	97,423	93,545	140 U
TR0701	112,383	117,822	113,453	99,796	33 J
TR1101	115,297	119,409	115,658	107,615	190 J
TR1201	112,650	123,548	116,120	109,747	44 J
TR1401	78,652	76,314	83,638	79,037	81.2 J
TR2601	97,873	93,763	99,026	96,446	72 J
TR3001	111,248	113,935	112,283	113,118	63 J
TR3101	112,868	115,630	113,189	107,695	37 J
TR3201	118,718	122,439	117,801	122,350	120 J
TR3601	127,292	128,690	124,368	117,178	250 J
TU0104	24,634	19,291	20,629	---	37 U
TU0203	12,040	121	153	---	3.2 UJ
TU0204	18,367	27,895	18,722	---	0.65 J
TU0301	5 U	6.8	7 U	---	3.6 UJ
TU0306	21,473	25,261	21,232	---	0.98 J
TU0405	300	248	330	---	3.3 UJ
TU0501	25	20	35	---	2.5 J
TU0504	1,620	1,406	1,724	---	3.3 U
TU0801	581	560	607	---	3.4 UJ
TU0902	104	2.5	5 U	4 U	3.6 UJ
TU0903	45	5 U	7.5	3.2	3.1 UJ
TU1404	6.8	4.7	4.6	---	2.7 UJ
TU2207	621	1,275	1,603	---	3.8 UJ
TU2503	316	117 U	250	---	1.5 UJ
TU3102	543	677	773	---	390 J
WM1004	18 U	7.7	37 U	---	3.5 UJ
WM1501	4 U	7 U	5 U	7 U	3.7 U
WM2203	5 U	2.9	3 U	14	4 UJ

U = undetected at level indicated. UJ = undetected at the level indicated; level is an estimate.
J = report result is an estimate. NJ = analyte was “tentatively identified” and reported result is approximate.