Study on the Applicability of X-ray Fluorescence Spectrometry for Use in ASTM F963 Total Element Screening

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This report was prepared by the CPSC staff, has not been reviewed or approved by, and may not necessarily reflect the views of, the Commission.

1.0 SUMMARY

The U.S Consumer Product Safety Commission ("CPSC") requires manufacturers and importers of children's products to certify that their products meet the requirements of ASTM F963-11[1], per the statutes of the Consumer Product Safety Improvement Act of 2008 (http://www.cpsc.gov/PageFiles/129663/cpsia.pdf).This standard limits the migration of heavy metals in the substrate materials of toys and toy parts. The heavy metals limited under this standard include antimony ("Sb"), arsenic ("As"), barium ("Ba"), cadmium ("Cd"), chromium ("Cr"), mercury ("Hg") and selenium ("Se"). The ASTM F963-11 standard test method for determining the soluble element content involves a 2-hour extraction in 0.07M hydrochloric acid and analysis of the extract solution by atomic spectroscopy. The standard also allows for total element content screening in which the test material is digested and analyzed by atomic spectroscopy, and if the total content of each of the elements is below the soluble limits prescribed, the material is considered to be in conformance with the standard, and no further testing is required. The test procedure for determining total element screening is less time-consuming than the test procedure for the soluble element content, and could likely be done for a lower cost. This report describes how X-ray fluorescence ("XRF") spectrometry potentially could be used for the total element content screening to test homogeneous plastic materials found in children's toys to determine compliance with the ASTM F963-11 standard.

CPSC evaluations of existing XRF spectrometry technologies demonstrate the potential, with certain limitations, to measure accurately Sb, As, Ba, Cd, Cr, Hg, and Se content in homogeneous plastic materials found in children's toys at the concentrations necessary to certify compliance with ASTM F963-11. A consensus standard test method for determining lead in homogeneous materials by energy dispersive XRF and appropriate reference materials containing lead in a variety of material types are already available. With the appropriate test methods and reference materials, XRF spectrometry is suitable, in many cases, for the determination of other elements in homogeneous materials.

A standard test method, ASTM F2853-10e1[2], for determining lead in homogeneous materials by energy dispersive XRF using multiple monochromatic beams, was developed by the ASTM International Committee F40 on Declarable Substances. Energy dispersive XRF using multiple monochromatic beams is more commonly referred to as high definition XRF or ("HDXRF").The standard and the interlaboratory research report[3] have been published and are available on the ASTM website, at: http://www.astm.org/Standards/F2853.htm. During 2014 and 2015, CPSC staff conducted additional testing of plastic samples and reference materials using HDXRF instrumentation, meeting the requirements of ASTM F2853-10e1, and using a portable handheld XRF analyzer ("HHXRF") to measure total element content of Sb, As, Ba, Cd, Cr, Hg, and Se. The results from using both XRF methods are detailed in this report and compared to other

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[1] ASTM F963-11 Standard Consumer Safety Specification for Toy Safety.

[2] ASTM F2853-10e1, Standard Test Method for Determination of Lead in Paint Layers and Similar Coatings or in Substrates and Homogeneous Materials by Energy Dispersive X-Ray Fluorescence Spectrometry Using Multiple Monochromatic Excitation Beams.

[3] ASTM Research Report F40-1001 Interlaboratory Study to Establish Precision Statements for ASTM F2853-10, July 1, 2010.

analytical techniques, such as Inductively-Coupled Plasma Optical Emission Spectrometry ("ICP"). This study was limited to evaluating the use of XRF techniques for determining the total element content of Sb, As, Ba, Cd, Cr, Hg, and Se in plastic materials.

This study determined that a specific type of XRF instrument, HD Prime, manufactured by X-ray Optical Systems Inc., a bench top energy dispersive XRF that uses multiple monochromatic excitation beams, is an HDXRF device that could accurately determine total element content in a variety of tested polymeric materials, including polyolefins and polyvinyl chloride. Other types of XRF instruments, such as the HHXRF, may be suitable for the total element content screening; but standard test methods and standard reference materials would need to be developed to validate that a particular HHXRF instrument is suitable for testing Sb, As, Ba, Cd, Cr, Hg, and Se in polymeric materials in the range of interest, with detection limits below the maximum soluble element limits listed in Table 1 of the ASTM F963-11.CPSC staff will provide this report to the ASTM F15 committee, along with specific recommendations to modify the F963 standard to allow for HDXRF use to make determinations of the elemental content of Sb, As, Ba, Cd, Cr, Hg, and Se in plastic materials.

2.0 SCOPE AND APPLICABILITY

2.1 Total Element Screening Analysis by Atomic Spectrometry

The current test method as outlined in 8.3.1 of ASTM F963-11 for determining total element content screening involves dissolving the toy material in *aqua regia* (three parts concentrated hydrochloric acid to one part concentrated nitric acid), and analyzing the diluted acid solution by spectroscopic means, such as ICP, inductively coupled plasma mass spectrometry ("ICP-MS"), flame atomic absorption spectrometry ("FLAA") or graphite furnace atomic absorption spectrometry ("GFAA"). These analytical techniques are capable of yielding precise and accurate results and have low enough detection limits to measure each element in the substrate to the limits prescribed in Table 1 of section 4 of ASTM F963-11. The method is time-consuming, typically requiring several hours to prepare and analyze samples and standards. The procedure is also sample destructive, requires the use of corrosive and poisonous acids, and generates hazardous waste containing those acids.

2.2 Potential Advantages of Using XRF for Homogeneous Substrate Analysis:

The main advantages of using XRF over the current digestion/ICP method for screening for total element content would be:

1. XRF analysis is often non-destructive for homogeneous materials.
2. Little to no sample preparation is required, which greatly reduces the analysis time and cost. Sample measurement times for XRF analysis are typically less than 5 minutes per measurement, versus several hours to cut, weigh, digest, and analyze using the current test method. The faster analysis times obtained using XRF would be expected to result in lower test costs.

3. XRF does not involve use of hazardous acids, so the costs of hazardous material disposal that are associated with current wet chemical methods are eliminated.
4. Some XRF analyzers are portable, allowing for field-screening of products.

2.3 Limitations of XRF Analysis:

Analysis of plastic toy part substrate materials for Sb, As, Ba, Cd, Cr, Hg, and Se that may be found in children's products by XRF have the following limitations:

1. Heterogeneous materials, such as painted plastic or layered material, may require some type of sample preparation to produce a homogeneous substrate specimen for quantitative XRF analysis.
2. XRF instruments generate x-ray radiation. This requires specialized training and safety precautions for the use of XRF, to maintain radiation safety during XRF use.
3. Spectral and matrix interferences must be taken into account during analysis. Spectral interferences result from spectral overlaps among the X-ray lines that are unresolved due to limited resolution of the detector. Some well-known overlaps include: As Kα peak directly overlapping lead (Pb) Lα peak, the sum peak of iron (Fe) Kα overlapping Pb Lβ peak, Se Kβ peak overlapping Pb Lβ peak. The XRF manufacturers' software may provide tools or de-convolution algorithms to compensate for these spectral interferences, but the precision of the analysis may be affected.
4. Plastic materials have a low x-ray absorption, which can lead to a requirement that specimens have a thickness of several millimeters to achieve infinite thickness to obtain accurate quantitative results. Many manufacturers of XRF spectrometers use algorithms that can correct for variations in the thickness of the specimen by means such as measuring x-ray scatter.

3.0 SUMMARY OF METHODS

3.1 XRF Instruments

The XRF instruments used in this study are property that CPSC currently owns. There are many types of XRF analyzers that come from different manufacturers, and CPSC does not endorse the instruments used in this study or any other. The purpose of this study was not to evaluate every XRF analyzer on the market, but to determine if it is feasible to use XRF to measure for the total element screening that is an option in the ASTM F963-11 standard. A description of the XRF instruments used in this study follows:

a. HD Prime, an HDXRF manufactured by X-ray Optical Systems Inc. Bench top energy dispersive XRF that uses multiple monochromatic excitation beams. The analyzer meets the requirements of ASTM F2853-10e1. The software allows the user to select the type of material analyzed, but measurement times and calibration are set by the manufacturer. The manufacturer provides reference materials to allow the user to verify calibration, but the user cannot make any changes to calibration parameters.

b. Thermo NITON XL3t 700, manufactured by Thermo Fisher Scientific. An HHXRF with a silicon drift detector. The software allows the user to select a few operating parameters, such as type of material analyzed, filter settings, and measurement time. There is also a system check option in the software that allows the user to perform a calibration of the detector's energy ("keV") scale. The manufacturer provides reference materials to allow the user to verify calibration, but the user cannot make changes to parameters in the empirical calibration provided by the manufacturer. The operating parameters selected for this study were:

    1. Measurement time – 300 seconds
    2. Filter – 60 seconds on main filter and 40 seconds on light filter.
    3. Sample type – *Consumer Goods/Test All*

3.2 ICP Calibration and Analysis

ICP calibration standards were prepared at 0.00, 0.10, 0.25, 0.50, 1.00, 5.00, and 10.0 parts per million ("ppm") by dilution of a 1000 µg/ml stock standards of As, Sb, Ba, Cd, Cr, Hg, and Se. A quality control standard at 0.50 µg/ml was prepared by the dilution of a 100 µg/ml multi-element standard SPEX CertiPrep, Metuchen NJ; Cat# QC-21. An internal standard of 2 µg/ml yttrium in 2% nitric acid was prepared using a 1000 µg/ml standard SPEX CertiPrep, Metuchen NJ; Cat# PLY-2Y.Standards, blanks, and samples were analyzed using the following conditions: a plasma flow 15.0L/min; nebulizer flow 0.75 L/min; pump speed 20 rpm; auxiliary flow 1.5 L/min; yttrium wavelength 324.228nm; power 1.30kW; and 4 replicates. The calibration curves had correlation coefficients greater than 0.999 with less than 10 percent error for the quality control standard.

3.3 Materials Tested

The materials evaluated in this study included plastic reference materials, plastic parts from consumer products, and a polyvinyl chloride material that was formulated by CPSC staff. The materials evaluated in this study were selected based on the known presence of one or more of the elements listed in ASTM F963-11 with limited soluble migrated element content. A description of materials is provided in Table 1.Table 2 provides the chemical identification of the material as determined by Fourier transform infrared spectrometry ("FTIR") and information on other non-ASTM F40 elements present, as determined by HDXRF.

Table 1. Sample and Reference Material Descriptions

Sample Identification	Description
680k	*Certified Reference Material ERM®-EC680k
681k	*Certified Reference Material ERM®-EC681k
GBW08404[4]	Research material from the National Institute of Metrology, China
GBW08405	Research material from the National Institute of Metrology, China
EN-71-3	Multi-element reference material plastic disk, lot 50, provided by Thermo Fisher Scientific in XRF carry case, Niton PN 180-619
RC1	Black plastic from remote control of toy RC car
4106R	Red plastic children's chair
4961GB	Green plastic toy boat
4960M	Green plastic mortar gun from toy soldier set
4960BP	Green plastic toy soldier backpack
2946W	Black plastic wheel from toy car
6592BP	Black plastic from toy kaleidoscope
4643C	Black plastic clip from children's backpack
2946T	Black plastic from toy truck
2949W	Black plastic wheel on toy motorcycle
2949H	Black plastic handlebar on toy motorcycle
3171PB	Children's Pink belt
3588TS	Pink plastic toe strap on children's sandal
3588HS	Pink plastic heel strap on children's sandal
3587TS	Blue plastic toe strap on children's sandal
3587HS	Blue plastic heel strap on children's sandal
3590B	Brown plastic sole on children's sole
3590TS	Purple plastic toe strap on children's sandal
3590HS	Purple plastic heel strap on children's sandal
PVC-L	**Polyvinyl chloride ("PVC") material containing total elemental concentrations of As, Sb, Cd, Cr, near 100 ppm and Ba and Se near the maximum soluble limit defined in ASTM F963-11.
PVC-H	**PVC material containing total elemental concentrations of As, Sb, Ba, Cd, Cr, Se 3-5 times higher than PVC-L.
PVC-.005-N2	NIST research material, PVC containing 50 ppm nominal concentration of Cd and Pb
PVC-0.01-N2	NIST research material, PVC containing 100 ppm nominal concentration of Cd and Pb
PVC-0.05-N2	NIST research material, PVC containing 500 ppm nominal concentration of Cd and Pb
PVC-0.1-N2	NIST research material, PVC containing 1000 ppm nominal concentration of Cd and Pb

*European Reference Material, polyethylene granules

** Material was formulated at facilities of the North Carolina Polymer Center of Excellence with CPSC staff on site adding the heavy metal elements to the PVC blend

[4] Certification of Reference Materials for Cr, Cr, Hg, and Pb in polypropylene by Liuxing Feng, Liandi Ma, Jun Wang, Hai Lu reported in Anal Bioanal Chem (2010) 396:3051–3057

Table 2. Plastic Type, Pb and Non-ASTM F963 Elements by HDXRF

Sample Identification	Plastic Type	Significant elements besides As, Sb, Ba, Cd, Cr, Hg, and Se detected by HDXRF or noted in Certificate of Analysis							
		Pb ppm	Br ppm	Fe ppm	Ca ppm	Si ppm	Sn ppm	Ti ppm	Zn ppm
680k	Polyethylene	14	96				15		137
681k	Polyethylene	98	770				86		1250
GBW08404	Polypropylene	96							
GBW08405	Polypropylene	913							
EN-71-3	Polyethylene	156							
RC1	Polystyrene/butadiene		367	242	4386			3478	
4106R	Polypropylene/ethylene			224	8821				
4961GB	Polypropylene/ethylene	389			133747	42299		3806	964
4960M	Polypropylene/ethylene	122	137	1918	129968	31251		5683	326
4960BP	Polypropylene/ethylene	128		2651	117506	30268		4556	253
2946W	Polypropylene/ethylene	225	211	5358	112317	40382		3743	681
6592BP	Polypropylene/ethylene		341	847	40816			1996	348
4643C	Polypropylene/ethylene		106	2945	115984	41195		3649	1121
2946T	Polypropylene/ethylene	163		2712	88181	32185	151	4531	390
2949W	Polypropylene/ethylene	157		3551	125684	36932		2786	380
2949H	Polypropylene/ethylene								
3171PB	PVC	368		174	81314			17874	564
3588TS	PVC	499			2588			1041	
3588HS	PVC	485			2441			815	
3587TS	PVC							577	
3587HS	PVC				237			564	
3590B	PVC	1814	421	6254	77661		161	2214	218
3590TS	PVC							640	
3590HS	PVC	527			2285			601	
PVC-L	PVC						886		
PVC-H	PVC						929		
PVC-.005-N2	PVC	56							
PVC-0.01-N2	PVC	123						90	
PVC-0.05-N2	PVC	524						527	
PVC-0.1-N2	PVC	950						1031	

4.0 RESULTS AND DISCUSSION

The ASTM F963-11 total element screening limits for elements other than Pb are listed in Table 3.If a toy material has total element content for the seven elements below the limit, the material is considered to be in conformance with the standard and no further testing is required. Tables 4-6 show the mean HDXRF, HHXRF, and ICP results for all the materials from Table 1, with results highlighted in bold for materials that exceed the total element screening limits. The HDXRF compared favorably to ICP in determining all instances in which an element was present in a material higher than the screening limits outlined in Table 3. Detailed comparisons of results for each element are provided in sections 4.1 to 4.7.

Table 3. Total Element Screening Limits in PPM (mg/kg) for Substrates Other Than Modeling Clay Included as Part of a Toy

Antimony (Sb)	Arsenic (As)	Barium (Ba)	Cadmium (Cd)	Chromium (Cr)	Mercury (Hg)	Selenium (Se)
60	25	1000	75	60	60	500

Table 4. Summary of Mean HDXRF Results

Sample ID	Sb (mg/kg)	As (mg/kg)	Ba (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Hg (mg/kg)	Se (mg/kg)
2946T	35.9	7	**13042**	1.8	ND	ND	ND
2946W	**62.7**	22.8	**8044**	5.5	**80.3**	ND	ND
2949H	32.6	18.5	**22370**	7	ND	ND	ND
2949W	38.4	18.9	**19368**	6.8	ND	ND	ND
3171PB	15.1	ND	591	**255**	ND	ND	ND
3587HS	10	ND	**1667**	**366**	ND	ND	ND
3587TS	11	ND	**1856**	**444**	ND	ND	ND
3588HS	10.4	6.5	392	**205**	ND	ND	ND
3588TS	11.3	ND	348	**207**	ND	ND	ND
3590B	**1385**	ND	338	**93.6**	**61.5**	ND	ND
3590HS	10.8	17.8	70	**151**	ND	ND	ND
3590TS	10.1	ND	**1249**	**384**	ND	ND	ND
4106R	ND	ND	31	**567**	ND	ND	79.3
4643C	**70**	18.3	**1605**	5.3	ND	ND	ND
4960BP	16.4	11.2	**14956**	ND	ND	ND	ND
4960M	49	**26.3**	**13683**	3.9	ND	ND	ND
4961GB	15.3	**25.7**	**49910**	**75.7**	ND	ND	ND
680k	11.5	4.2	4	20.3	18.4	4.8	ND
681k	**106**	**26.2**	74.2	**130**	**91.9**	33.1	1.1
6952BP	**132**	3.9	**1152**	ND	4.4	ND	ND
EN-71-3	**93.7**	**47.3**	786	**259**	**96.3**	**111**	178
GBW08404	ND	ND	230	**87.4**	**92.2**	**108**	ND
GBW08405	ND	ND	**2189**	8.5	**884**	**1076**	ND
PVC-H	**517**	**385**	**5958**	**270**	**438**	NI	**3412**
PVC-L	**125**	**94.4**	**1677**	**99.4**	**74.5**	NI	**753**
RC1	**187**	ND	ND	6	59.3	ND	ND
PVC-.005-N2	NT	NT	NT	58.2	NT	NT	NT
PVC-0.01N2	NT	NT	NT	**124**	NT	NT	NT
PVC-0.05N2	NT	NT	NT	**519**	NT	NT	NT
PVC-0.01N2	NT	NT	NT	**1005**	NT	NT	NT

NT = Not Tested

ND= Not Detected

NI=Hg results for PVC-H and PVC-L not included due to volatility of Hg, which resulted in Hg not being homogeneously dispersed in the materials

Table 5. Summary of Mean HHXRF Results

Sample ID	Sb (mg/kg)	As (mg/kg)	Ba (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Hg (mg/kg)	Se (mg/kg)
2946T	**31.8**	**1.8**	**10986**	10.8	ND	ND	ND
2946W	**95.9**	**ND**	**9206**	ND	**ND**	ND	ND
2949H	**20.4**	**ND**	**15842**	ND	ND	ND	ND
2949W	**19.9**	**ND**	**16090**	ND	ND	ND	ND
3171PB	ND	ND	**712**	**113**	ND	ND	ND
3587HS	ND	ND	**628**	**178**	ND	ND	ND
3587TS	ND	ND	**692**	**228**	ND	ND	ND
3588HS	ND	ND	**149**	96.1	ND	ND	ND
3588TS	ND	ND	**169**	**101**	ND	ND	ND
3590B	**998**	ND	544	**52.8**	**7.1**	ND	ND
3590HS	ND	**ND**	58	**43.7**	ND	ND	ND
3590TS	ND	ND	**506**	**182**	ND	ND	ND
4106R	ND	1.9	122	**525**	ND	ND	**ND**
4643C	**73.7**	**7.2**	**2780**	3.5	ND	ND	ND
4960BP	**4.6**	**7.2**	**12034**	ND	ND	ND	ND
4960M	**44.6**	**10.4**	**24455**	ND	ND	ND	ND
4961GB	**8.8**	ND	**27658**	**77**	ND	ND	ND
680k	**6.3**	**5.5**	ND	**17.1**	**30.7**	**4.9**	ND
681k	**87.3**	**35.3**	**90**	**119**	**128**	**33**	ND
6952BP	**126**	**11.9**	**1274**	ND	ND	ND	ND
EN-71-3	**96.5**	**53.3**	**661**	**268**	**116**	**103**	**210**
GBW08404	ND	5.2	**201**	**78.9**	**124**	**116**	ND
GBW08405	ND	38.1	**1512**	**7**	**1020**	**1037**	ND
PVC-H	**388**	**532**	**3555**	**162**	**445**	ND	**5551**
PVC-L	**68.2**	**126**	**940**	**9.6**	**86.2**	NA	**1135**
RC1	**165**	4.5	191	ND	**199**	NA	ND
PVC-.005-N2	NT	NT	NT	**49**	NT	NT	NT
PVC-0.01N2	NT	NT	NT	**120**	NT	NT	NT
PVC-0.05N2	NT	NT	NT	**547**	NT	NT	NT
PVC-0.01N2	NT	NT	NT	**1054**	NT	NT	NT

Table 6. Summary of Mean ICP Results

Sample ID	Sb (mg/kg)	As (mg/kg)	Ba (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Hg (mg/kg)	Se (mg/kg)
2946T	**5**	**6.7**	**11314**	ND	NT	NT	ND
2946W	**51.6**	**15.8**	**7165**	0.6	NT	NT	6.4
2949H	**32**	**12.5**	**10850**	ND	NT	NT	ND
2949W	**32.7**	**13.2**	**11510**	ND	NT	NT	ND
3171PB	6.4	5.4	**2039**	**262**	NT	NT	7.4
3587HS	ND	1.9	**1218**	**314**	NT	NT	ND
3587TS	ND	ND	**1490**	**389**	NT	NT	ND
3588HS	8.1	ND	**231**	**170**	NT	NT	ND
3588TS	ND	ND	**242**	**171**	NT	NT	ND
3590B	**1428**	7.2	479	**72.3**	NT	NT	6.6
3590HS	6	**2.9**	48	**131**	NT	NT	7.5
3590TS	5.1	ND	**1073**	**327**	NT	NT	ND
4106R	ND	ND	30	**629**	NT	NT	**85**
4643C	**68.8**	**20**	**1862**	2.7	NT	NT	5.5
4960BP	**12.3**	**13.1**	**10213**	ND	NT	NT	6.4
4960M	**34.2**	**27.1**	**10637**	ND	NT	NT	6.9
4961GB	**1.2**	**21.7**	**10625**	**68.7**	NT	NT	ND
680k	**9.1**	**2.1**	9.7	**22.3**	NT	NT	ND
681k	**106**	**24.3**	**60.4**	**128**	NT	NT	1.1
6952BP	**107**	**9.7**	**1691**	0.6	NT	NT	7.1
EN-71-3	**111**	**46**	**669**	**282**	NT	NT	**203**
GBW08404	6.1	2.7	**199**	**81**	NT	NT	6.7
GBW08405	ND	ND	**1893**	**6.7**	NT	NT	ND
PVC-H	**538**	**467**	**4922**	**248**	NT	NT	**3188**
PVC-L	**121**	**107**	**1530**	**86.5**	NI	NI	**695**
RC1	**145**	ND	158	ND	NI	NI	ND
PVC-.005-N2	NT	NT	NT	**47.9**	NT	NT	NT
PVC-0.01N2	NT	NT	NT	**106**	NT	NT	NT
PVC-0.05N2	NT	NT	NT	**467**	NT	NT	NT
PVC-0.01N2	NT	NT	NT	**904**	NT	NT	NT

4.1 Antimony (Sb)

Table 7 compares results for Sb concentration obtained using the HDXRF, HHXRF, and ICP on the sample and reference materials. The certified or expected values noted on certificates are also displayed for the reference materials. The known amount of added Sb for the materials PVC-L and PVC-H are displayed in the same column. These certified or known amounts of elements added to the reference materials shall be referred to as reference amounts for convenience throughout the remainder of this report. At least four measurements were obtained on different locations on materials. The mean and standard deviations ("stdev") are included in the tables. Measurement results below ICP detection limits or denoted as not detected ("ND") by HHXRF or HDXRF are recorded as ND in the data tables. Figure 1 shows the correlation between the mean Sb concentration measurements obtained by ICP and HDXRF. Figure 2 shows the correlation between the mean Sb concentration measurements obtained by ICP and HHXRF. The R^2 coefficients may be artificially close to 1.0 due to the two much higher concentration points. Figures 3 and 4 show the correlations with those two points dropped.

The HDXRF and HHXRF Sb measurement results generally compare favorably with the ICP Sb results obtained for the samples. The HDXRF and HHXRF Sb measurement results obtained on the sample materials with ICP Sb results >10 ppm are usually within ±30% of ICP results with the following exceptions:

a. The PVC-L sample HHXRF Sb result was approximately 40 percent lower than the ICP Sb result.

b. The 2946W sample HHXRF Sb result was approximately 90 percent higher than the ICP Sb result.

ASTM F963-11 maximum soluble limit for Sb is 60 ppm. If a material screens higher than 60 ppm total Sb, the extraction test is required. The HDXRF and HHXRF successfully identified all the samples that had Sb above 60 ppm, as determined by ICP.

Figure 1

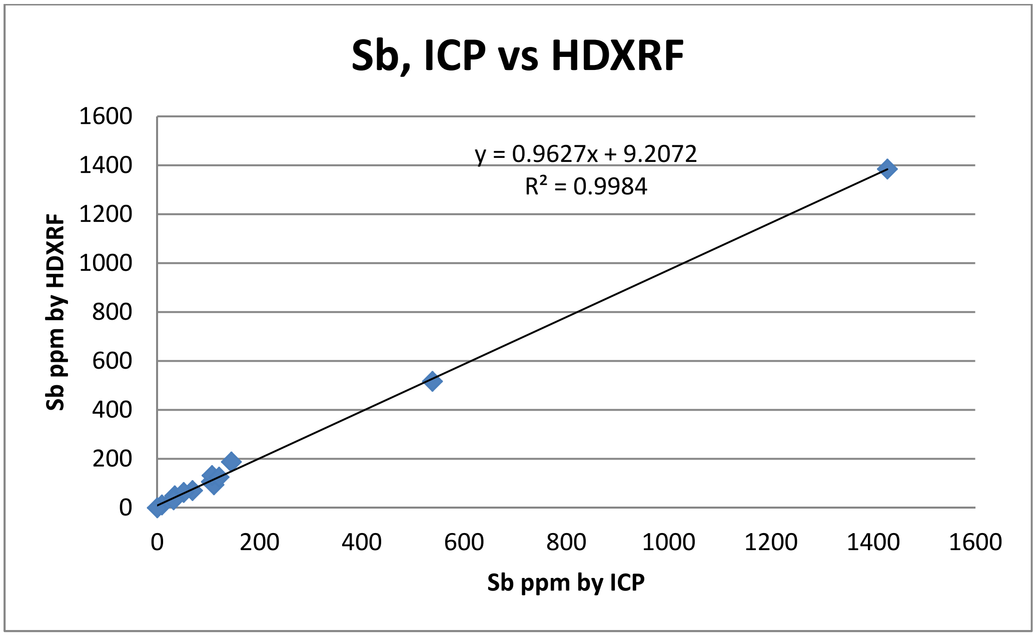

Figure 2

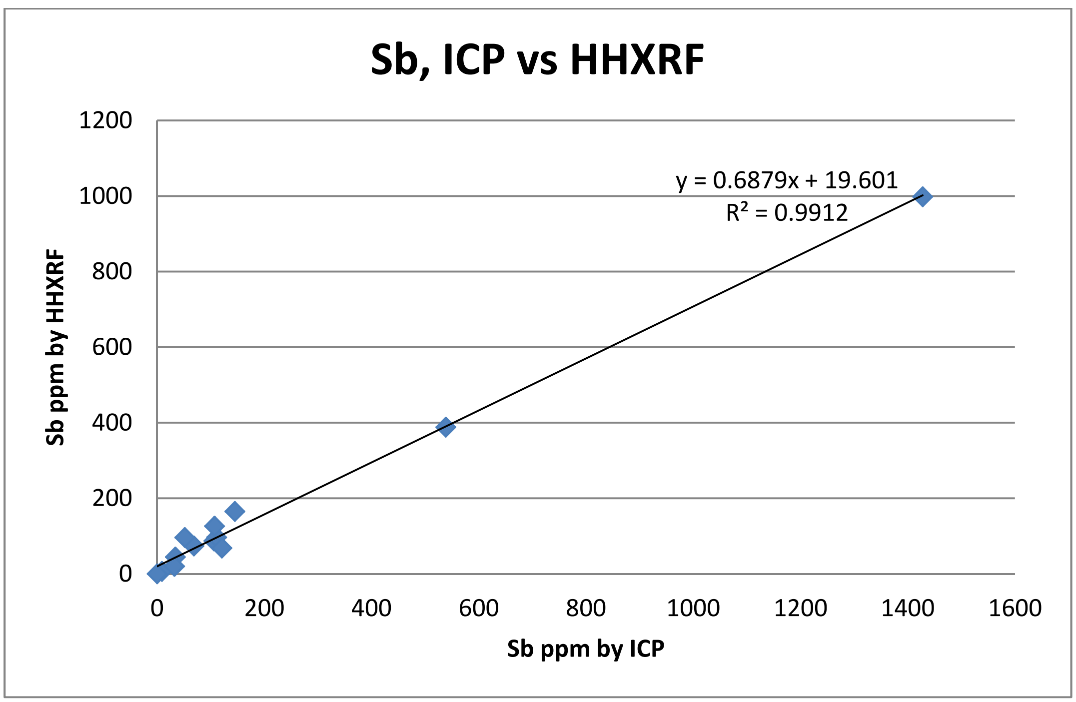

Figure 3. Materials with Sb <200 ppm

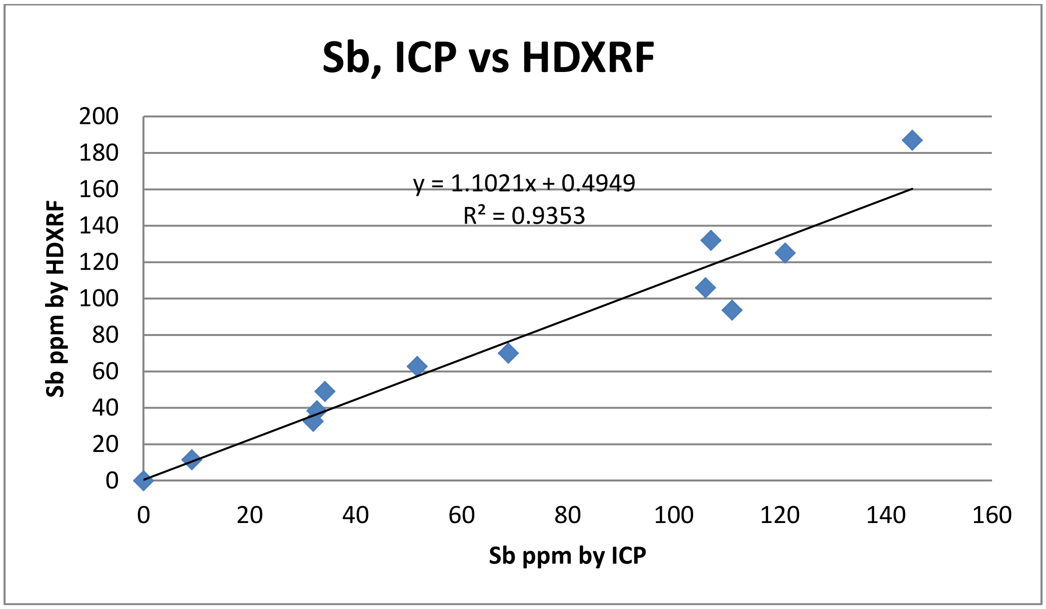

Figure 4. Materials with Sb <200 ppm

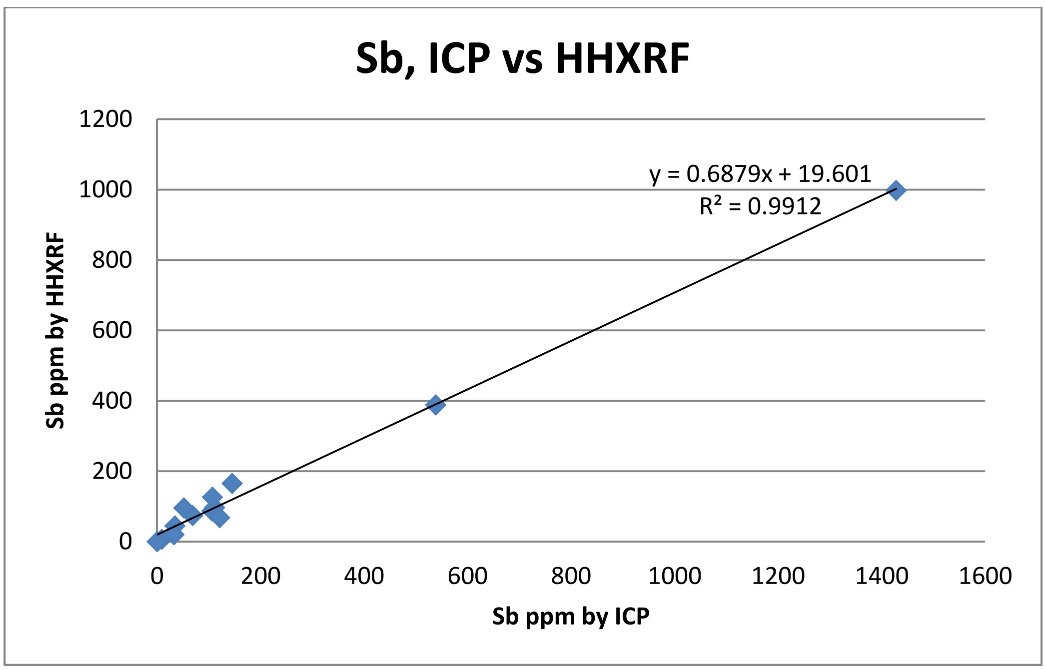

Table 7. Analysis of Materials for Sb

Sample ID	Replicate	HDXRF Sb mg/kg	HHXRF Sb mg/kg	ICP Sb mg/kg	Certified or Added amount of Sb mg/kg
680k	1	ND	12.5	14.1	**10.1**
	2	16	ND	7.9	
	3	15.4	12.8	7.0	
	4	14.4	ND	7.3	
	mean	**11.5**	**6.3**	**9.1**	
	stdev	**7.7**	**7.3**	**3.4**	
681k	1	106	88.0	112	**99**
	2	105	92.0	102	
	3	106	84.0	106	
	4	107	85.0	104	
	mean	**106**	**87.3**	**106**	
	stdev	**0.8**	**3.6**	**4.4**	
GBW08404	**mean**	ND	ND	6.1	
GBW08405	**mean**	ND	ND	ND	
EN-71-3	1	85.6	96.8	120	**102**
	2	96.5	97.3	114	
	3	98.9	99.5	91.5	
	4	93.8	92.4	116	
	mean	**93.7**	**96.5**	**111**	
	stdev	**5.8**	**3.0**	**13.0**	
4961GB	1	17.7	17.3	4.7	
	2	24.7	ND	ND	
	3	ND	ND	ND	
	4	18.7	18.0	ND	
	mean	**15.3**	**8.8**	**1.2**	
	stdev	**10.6**	**10.2**	**2.3**	
4960M	1	51.9	47.1	50.9	
	2	51.0	42.0	18.4	
	3	49.3	48.9	50.0	
	4	43.9	40.5	17.4	
	mean	**49.0**	**44.6**	**34.2**	
	stdev	**3.6**	**4.0**	**18.8**	
4960BP	1	ND	ND	11.5	
	2	22.8	18.5	11.8	
	3	21.3	ND	11.2	
	4	21.5	ND	14.6	
	mean	**16.4**	**4.6**	**12.3**	
	stdev	**11.0**	**9.2**	**1.6**	

Note: ASTM F963-11 Sb total element screening limit is 60ppm

Table 7. Continued. Analysis of Materials for Sb

Sample ID	Replicate	HDXRF Sb mg/kg	HHXRF Sb mg/kg	ICP Sb mg/kg	Certified or Added amount of Sb mg/kg
2946T	1	31.7	27.2	6.0	
	2	39.5	34.5	4.5	
	3	31.9	27.4	8.8	
	4	40.3	38.2	0.8	
	mean	**35.9**	**31.8**	**5.0**	
	stdev	**4.7**	**5.5**	**3.3**	
6952BP	1	136	137	104	
	2	146	111	100	
	3	121	128	109	
	4	127	126	114	
	mean	**132**	**126**	**107**	
	stdev	**10.9**	**10.5**	**6.1**	
4643C	1	69.1	74.9	72.6	
	2	76.6	53.5	66.6	
	3	79.8	98.4	63.8	
	4	54.6	67.8	72.2	
	mean	**70.0**	**73.7**	**68.8**	
	stdev	**11.2**	**18.7**	**4.3**	
2946W	1	81.5	95.8	44.3	
	2	98.1	96.9	45.0	
	3	28.1	95.0	68.2	
	4	62.9	95.9	48.8	
	mean	**62.7**	**95.9**	**51.6**	
	stdev	**30.0**	**0.8**	**11.3**	
2949W	1	44.1	ND	32.0	
	2	55.5	24.2	31.8	
	3	25.7	24.2	34.0	
	4	28.3	31.1	33.2	
	mean	**38.4**	**19.9**	**32.7**	
	stdev	**14.0**	**13.6**	**1.0**	
2949H	1	29.7	26.5	31.8	
	2	38.5	29.9	33.8	
	3	32.7	25.0	30.4	
	4	29.6	ND	32.1	
	mean	**32.6**	**20.4**	**32.0**	
	stdev	**4.2**	**13.7**	**1.4**	
3171PB	**mean**	15.1	ND	6.4	
3588TS	**mean**	11.3	ND	ND	
3588HS	**mean**	10.4	ND	8.1	
3587TS	**mean**	11.0	ND	ND	
3587HS	**mean**	10.0	ND	ND	
3590HS	**mean**	10.8	ND	6.0	
3590TS	**mean**	10.1	ND	5.1	

Table 7 Continued. Analysis of Materials for Sb

Sample ID	Replicate	HDXRF Sb mg/kg	HHXRF Sb mg/kg	ICP Sb mg/kg	Certified or Added amount of Sb mg/kg
3590B	1	1397	956.8	1428	
	2	1328	1044	1400	
	3	1372	949	1525	
	4	1444	1040	1359	
	mean	**1385**	**998**	**1428**	
	stdev	**48.4**	**51.5**	**71.0**	
PVC-L	1	137	71	121	107
	2	127	69	122	
	3	129	68	123	
	4	117	68	118	
	5	116	65	121	
	mean	**125**	**68.2**	**121**	
	stdev	**8.8**	**2.2**	**2.1**	
PVC-H	1	524	388	548	526
	2	526	384	534	
	3	515	388	535	
	4	517	392	541	
	5	503	389	533	
	mean	**517**	**388**	**538**	
	stdev	**9.0**	**2.9**	**6.4**	
RC1	1	204	155	141	
	2	177	175	131	
	3	189	161	157	
	4	177	168	150	
	mean	**187**	**165**	**145**	
	stdev	**12.8**	**8.8**	**11.3**	
4106R	**mean**	ND	ND	ND	

4.2 Arsenic (As)

Table 8 compares results for As concentration obtained using the HDXRF, HHXRF, and ICP on the sample and reference materials. The certified or expected values noted on certificates are also displayed. At least four measurements were obtained on different locations on materials. The mean and stdev are included in the tables. Figure 5 shows the correlation between the mean As concentration measurements obtained by ICP and HDXRF. Figure 6 shows the correlation between the mean As concentration measurements obtained by ICP and HHXRF.

The HDXRF and HHXRF As measurement results generally compare favorably with the ICP As results obtained for the samples. The HDXRF and HHXRF As measurement results obtained on the sample materials with ICP As results >20 ppm are usually within ±30% of ICP results with the following exceptions:

a. The 681k sample HHXRF As result was approximately 40 percent higher than the ICP As result.
b. HHXRF was unable to detect As in a number of the samples with ICP As results in the 10−25 ppm range.

ASTM F963-11 maximum soluble limit for As is 25 ppm. If a material screens higher than 25 ppm total As, the extraction test is required. The HDXRF successfully identified all the samples that had As above 25 ppm, as determined by ICP. The HHXRF successfully identified all the samples that had As above 25 ppm, except for 4960B sample. The mean ICP As result for 4960B was 27 ppm, just over the 25 ppm limit. The mean HHXRF result for 4960B was 10 ppm.

Figure 5

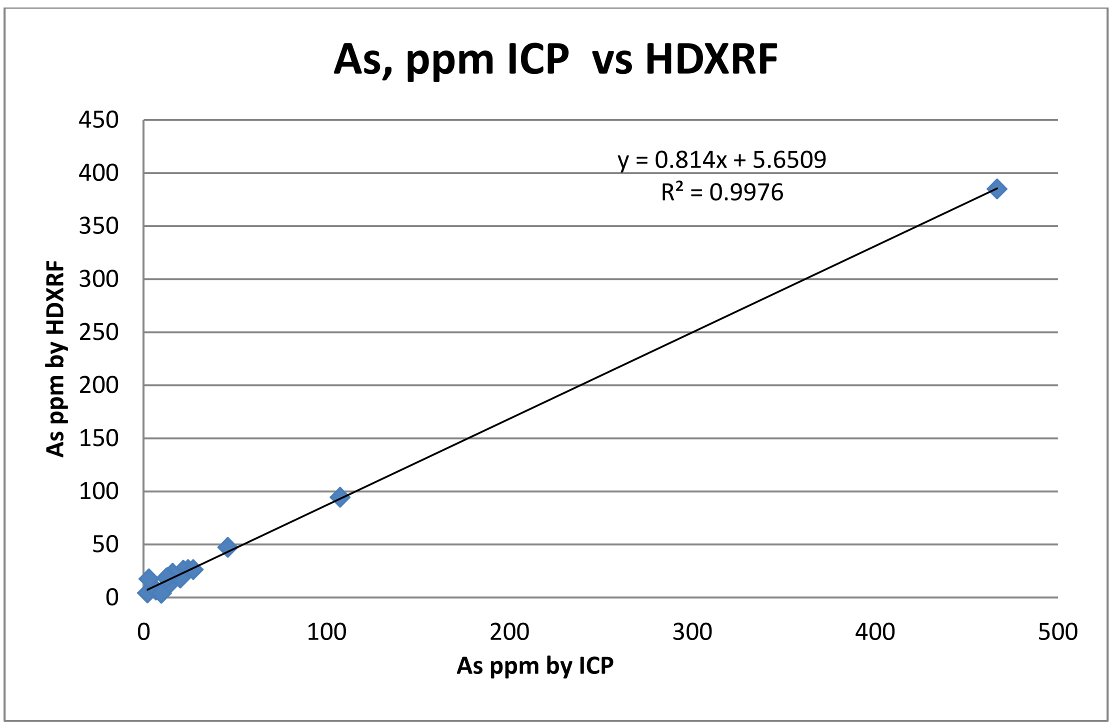

Figure 6

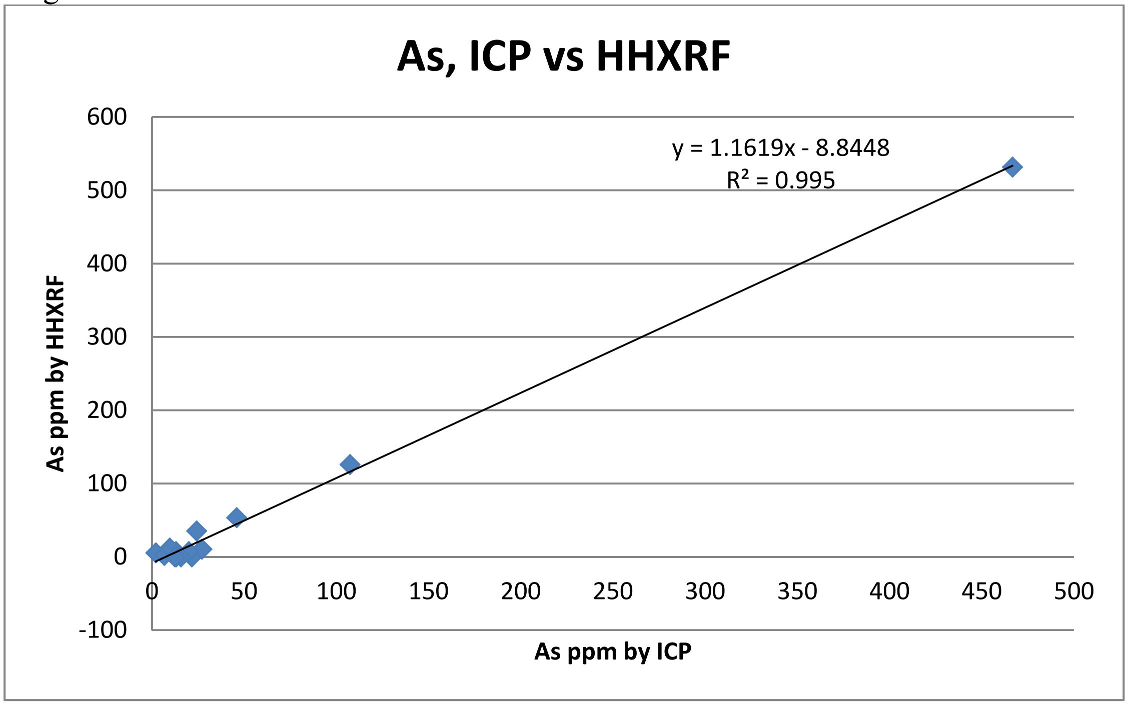
As, ICP vs HHXRF
y = 1.1619x - 8.8448
R² = 0.995
As ppm by HHXRF
As ppm by ICP
600
500
400
300
200
100
0
-100
0
50
100
150
200
250
300
350
400
450
500

Table 8. Analysis of Materials for As

Sample ID	Replicate	HDXRF As mg/kg	HHXRF As mg/kg	ICP As mg/kg	Certified or Added amount of As mg/kg
680k	1	3.7	6.0	4.5	**4.1**
	2	3.9	5.0	2.3	
	3	4.6	5.6	1.4	
	4	4.6	5.4	ND	
	mean	**4.2**	**5.5**	**2.1**	
	stdev	**0.5**	**0.4**	**1.9**	
681k	1	23.6	33.6	25.4	**29.1**
	2	25.3	36.4	23.4	
	3	26.8	34.5	25.1	
	4	29.0	36.5	23.4	
	mean	**26.2**	**35.3**	**24.3**	
	stdev	**2.3**	**1.4**	**1.1**	
GBW08404	**mean**	ND	5.2	2.7	
GBW08405	**mean**	ND	38.1	ND	
EN-71-3	1	44.5	52.3	49.0	**51**
	2	42.2	54.0	49.3	
	3	52.0	52.8	38.3	
	4	50.5	54.1	47.2	
	mean	**47.3**	**53.3**	**46.0**	
	stdev	**4.7**	**0.9**	**5.2**	
RC1	**mean**	ND	4.5	ND	
4106R	**mean**	ND	1.9	ND	
4961GB	1	28.6	ND	24.0	
	2	21.6	ND	20.7	
	3	41.4	ND	21.6	
	4	11.3	ND	20.7	
	mean	**25.7**		**21.7**	
	stdev	**12.6**		**1.5**	
4960M	1	23.0	7.4	28.1	
	2	31.5	8.8	26.5	
	3	29.6	14.1	27.8	
	4	21.1	11.2	26.2	
	mean	**26.3**	**10.4**	**27.1**	
	stdev	**5.0**	**2.9**	**0.9**	
4960BP	1	11.1	ND	12.4	
	2	10.1	9.2	12.7	
	3	17.6	9.8	13.4	
	4	6.0	9.6	13.7	
	mean	**11.2**	**7.2**	**13.1**	
	stdev	**4.8**	**4.8**	**0.6**	

Note: ASTM F963-11 As total element screening limit is 25ppm

Table 8 Continued. Analysis of Materials for As

Sample ID	Replicate	HDXRF As mg/kg	HHXRF As mg/kg	ICP As mg/kg	Certified or Added amount of As mg/kg
2946T	1	5.2	7.2	4.3	
	2	8.8	ND	12.5	
	3	7.7	ND	4.7	
	4	6.4	ND	5.4	
	mean	**7.0**	**1.8**	**6.7**	
	stdev	**1.6**	**3.6**	**3.9**	
6952BP	1	ND	13.8	9.0	
	2	4.1	12.0	9.0	
	3	5.9	8.7	10.3	
	4	5.6	13.2	10.5	
	mean	**3.9**	**11.9**	**9.7**	
	stdev	**2.7**	**2.3**	**0.8**	
4643C	1	17.6	ND	21.2	
	2	13.7	13.2	19.3	
	3	18.5	5.9	20.9	
	4	23.5	10.0	18.5	
	mean	**18.3**	**7.2**	**20.0**	
	stdev	**4.0**	**5.7**	**1.3**	
2946W	1	28.7	ND	15.8	
	2	18.2	ND	14.8	
	3	20.3	ND	17.0	
	4	23.8	ND	15.6	
	mean	**22.8**	**ND**	**15.8**	
	stdev	**4.6**		**0.9**	
2949W	1	10.1	ND	12.5	
	2	27.1	ND	12.4	
	3	19.3	ND	12.1	
	4	18.9	ND	15.9	
	mean	**18.9**	**ND**	**13.2**	
	stdev	**6.9**		**1.8**	
2949H	1	21.5	ND	12.7	
	2	15.3	ND	13.0	
	3	9.9	ND	12.7	
	4	27.2	ND	11.7	
	mean	**18.5**	**ND**	**12.5**	
	stdev	**7.5**		**0.6**	

Table 8 Continued. Analysis of Materials for As

Sample ID	**Replicate**	**HDXRF As mg/kg**	**HHXRF As mg/kg**	**ICP As mg/kg**	**Certified or Added amount of As mg/kg**
3171PB	**mean**	ND	ND	5.4	
3588TS	**mean**	ND	ND	ND	
3588HS	**mean**	6.5	ND	ND	
3587TS	**mean**	ND	ND	ND	
3587HS	**mean**	ND	ND	1.9	
3590B	**mean**	ND	ND	7.2	
3590HS	1	22.6	ND	2.1	
	2	12.2	ND	2.1	
	3	ND	ND	3.2	
	4	36.5	ND	4.0	
	mean	**17.8**	**ND**	**2.9**	
	stdev	**15.5**		**0.9**	
3590TS	**mean**	ND	ND	ND	
PVC-L	1	105	129	102	101
	2	89.1	135	106	
	3	93.5	119	119	
	4	92.4	118	107	
	5	92.2	128	103	
	mean	**94.4**	**126**	**107**	
	stdev	**6.1**	**7.2**	**7.1**	
PVC-H	1	373	508	462	454
	2	359	529	510	
	3	378	509	428	
	4	418	576	450	
	5	397	536	483	
	mean	**385**	**532**	**467**	
	stdev	**22.9**	**27.7**	**31.5**	

4.3 Barium (Ba)

Table 9 compares results for Ba concentration obtained using the HDXRF, HHXRF, and ICP on the sample and reference materials. The certified or expected values noted on certificates are also displayed. At least four measurements were obtained on different locations on materials. The mean and stdev are included in the tables. Figure 7 shows the correlation between the mean Ba concentration measurements obtained by ICP and HDXRF on samples with less than 10000ppm Ba by ICP. Figure 8 shows the correlation between the mean Ba concentration measurements obtained by HDXRF and the reference amounts of Ba for the reference materials. Figure 9 shows the correlation between the mean Ba concentration measurements obtained by ICP and HHXRF on samples with less than 10000ppm Ba by ICP. Figure 10 shows the correlation between the mean Ba concentration measurements obtained by HHXRF and the referenced amounts of Ba reported for the reference materials.

Many of the sample materials evaluated in this study contained high levels of Ba, greater than 10,000 ppm.The higher relative standard deviations for Ba of many of the sample materials indicate some of the materials may be less homogeneous with respect to Ba. Both the HDXRF and HHXRF results had better correlations with the referenced Ba for the reference materials than the Ba ICP results for the sample materials, which may be due to lack of homogeneity of Ba in the samples and high levels of Ba detected in many of the samples. The ASTM F963-11 maximum soluble limit for Ba is 1000 ppm. If a material screens higher than 1000 ppm total Ba, the extraction test is required. The HDXRF successfully identified all the samples that had Ba above 1000 ppm, as determined by ICP, except for sample 3171PB. Based on ICP and HDXRF results, 3171PB sample material does not appear to be homogeneous with respect to Ba, which may explain some of the discrepancies between the ICP and HDXRF Ba results. The HHXRF successfully identified all the samples that had Ba above 1000 ppm, as determined by ICP, except for 3171PB, 3587TS, 3587HS, 3590TS, and PVC-L.

Figure 7

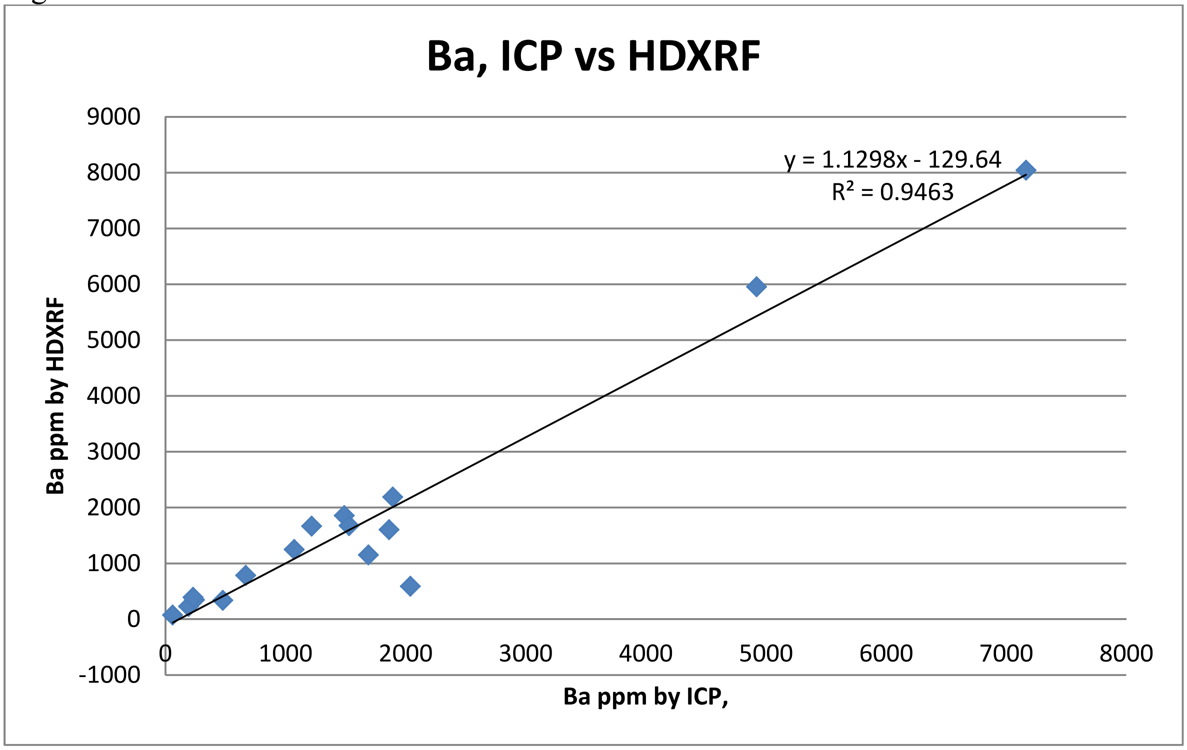

Figure 8

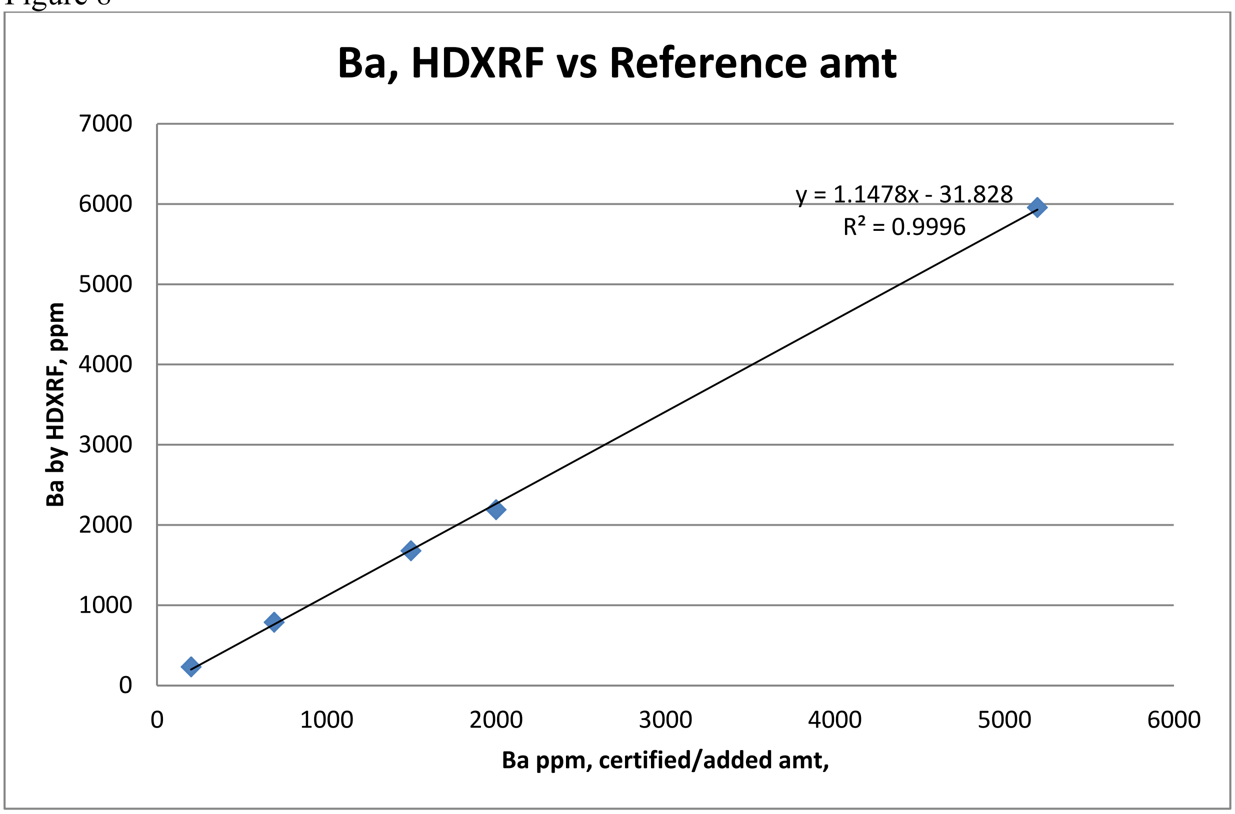

Figure 9

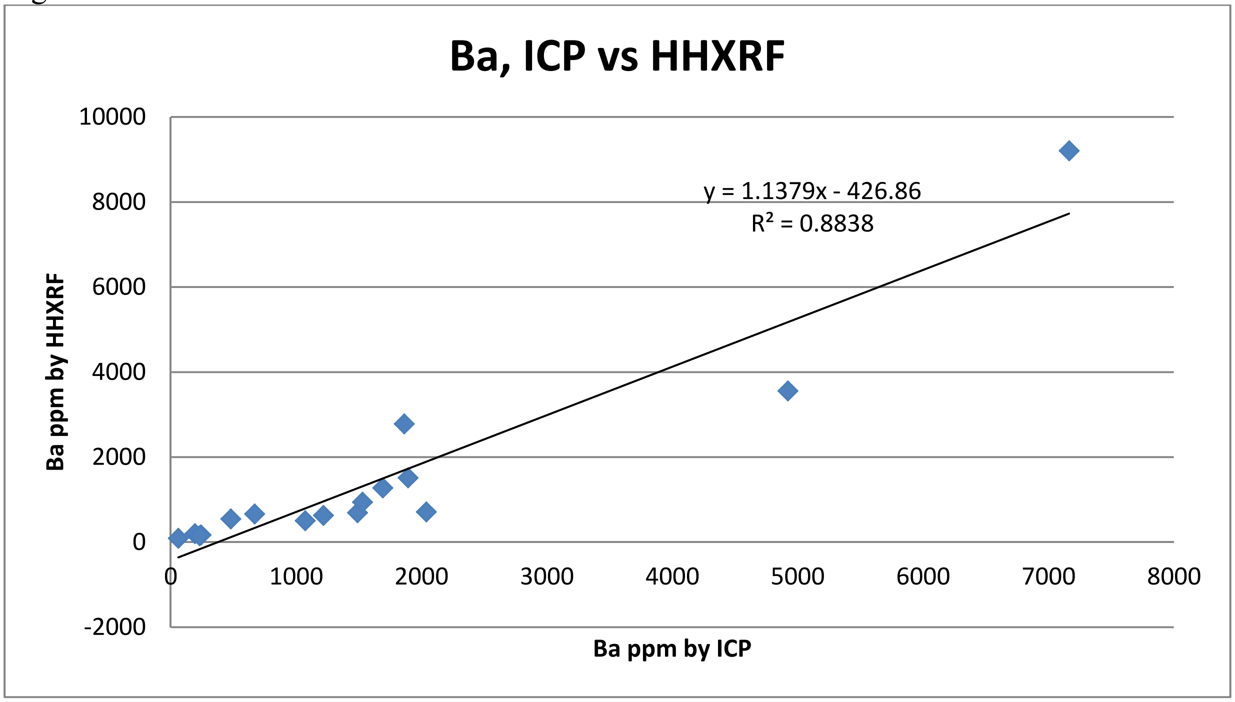

Figure 10

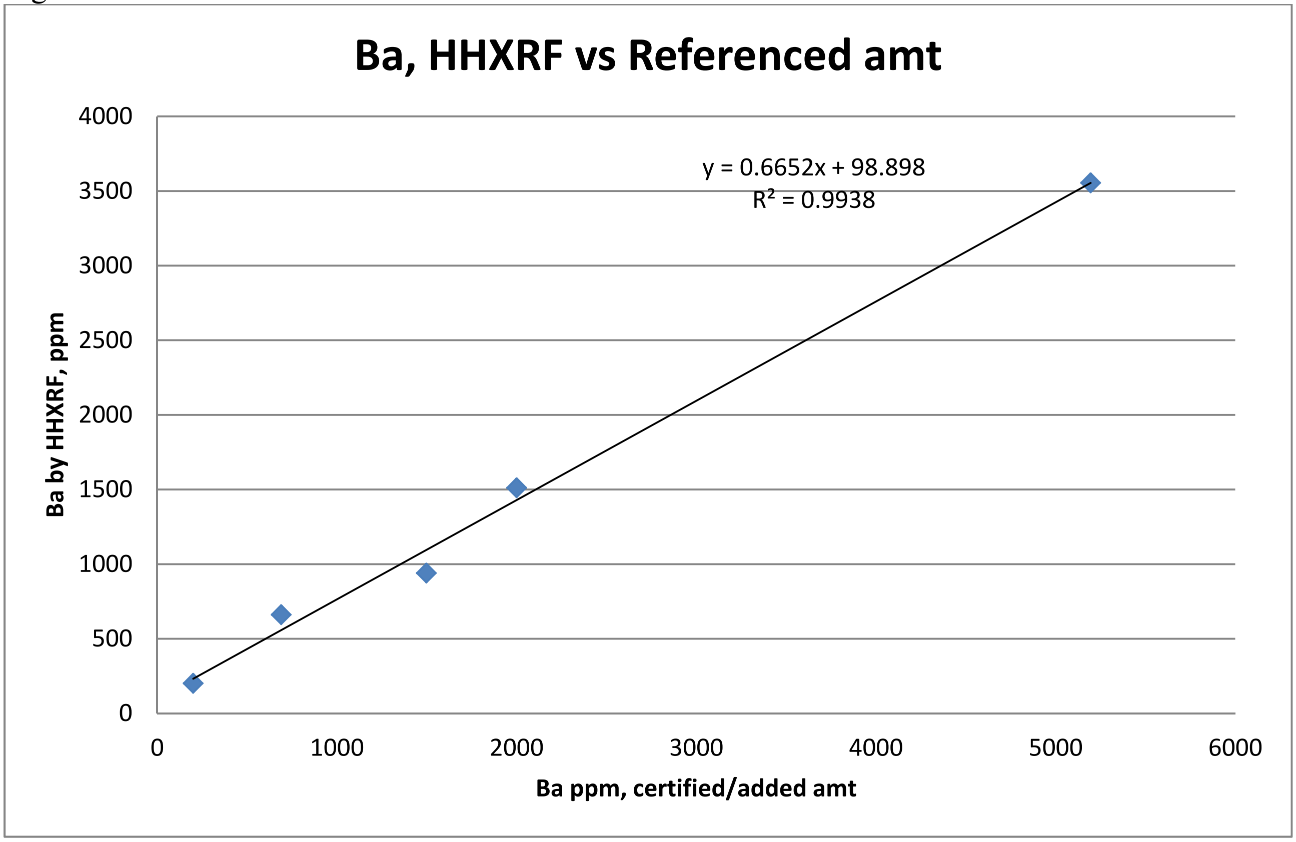

Table 9. Analysis of Materials for Ba

Sample ID	Replicate	HDXRF Ba mg/kg	HHXRF Ba mg/kg	ICP Ba mg/kg	Certified or Added amount of Ba mg/kg
680k	**mean**	4.0	ND	9.7	
681k	1	67.3	110.0	64.2	
	2	79.0	101.0	59.2	
	3	75.9	80.0	59.5	
	4	74.7	69.0	58.7	
	mean	**74.2**	**90.0**	**60.4**	
	stdev	**5.0**	**18.8**	**2.6**	
GBW08404	1	217	206	173	**200**
	2	234	188	176	
	3	237	201	174	
	4	233	208	271	
	mean	**230**	**201**	**199**	
	stdev	**9.0**	**9.2**	**48.4**	
GBW08405	1	2155	1517	1931	**2000**
	2	2215	1497	1942	
	3	2228	1519	1772	
	4	2157	1518	1928	
	mean	**2189**	**1512**	**1893**	
	stdev	**38.2**	**10.3**	**80.9**	
EN-71-3	1	770	656	726	**690**
	2	764	678	700	
	3	796	676	532	
	4	815	633	718	
	mean	**786**	**661**	**669**	
	stdev	**23.7**	**20.9**	**91.9**	
RC1	**mean**	ND	191	158	
4106R	**mean**	31	122	30	
4961GB	1	49968	28081	8760	
	2	53104	27422	8918	
	3	50907	27113	9956	
	4	45663	28013	14866	
	mean	**49910**	**27658**	**10625**	
	stdev	**3121**	**468**	**2877**	
4960M	1	13667	24748	9750	
	2	14740	24204	11171	
	3	14018	26041	11218	
	4	12308	22828	10408	
	mean	**13683**	**24455**	**10637**	
	stdev	**1020**	**1331**	**698**	

Note: ASTM F963-11 Ba total element screening limit is 1000 ppm

Table 9 Continued. Analysis of Materials for Ba

Sample ID	Replicate	HDXRF Ba mg/kg	HHXRF Ba mg/kg	ICP Ba mg/kg	Certified or Added amount of Ba mg/kg
4960BP	1	14602	12429	10742	
	2	13492	12044	9133	
	3	17722	11700	10223	
	4	14007	11964	10756	
	mean	**14956**	**12034**	**10213**	
	stdev	**1899**	**302**	**762**	
2946T	1	12894	10920	10942	
	2	13502	10963	10268	
	3	13103	11071	9940	
	4	12667	10989	14109	
	mean	**13042**	**10986**	**11314**	
	stdev	**355**	**64**	**1909**	
6952BP	1	976	1283	1694	
	2	1357	1253	1737	
	3	1219	1317	1682	
	4	1056	1243	1649	
	mean	**1152**	**1274**	**1691**	
	stdev	**170**	**33.1**	**36.7**	
4643C	1	1325	3321	2003	
	2	1704	1879	1944	
	3	1583	3651	1783	
	4	1809	2267	1719	
	mean	**1605**	**2780**	**1862**	
	stdev	**208**	**842**	**133**	
2946W	1	6416	8819	6744	
	2	5950	9377	6842	
	3	9675	9445	7713	
	4	10133	9183	7363	
	mean	**8044**	**9206**	**7165**	
	stdev	**2165**	**281**	**455**	
2949W	1	17670	36358	11836	
	2	21825	9176	10727	
	3	16458	9278	14316	
	4	21519	9546	9161	
	mean	**19368**	**16090**	**11510**	
	stdev	**2709**	**13513**	**2169**	
3588TS	**mean**	**348**	**169**	**242**	
3588HS	**mean**	**392**	**149**	**231**	
3590B	**mean**	338	544	479	
3590HS	**mean**	70	58	48	

Table 9 Continued. Analysis of Materials for Ba

Sample ID	Replicate	HDXRF Ba mg/kg	HHXRF Ba mg/kg	ICP Ba mg/kg	Certified or Added amount of Ba mg/kg
2949H	1	21767	10148	11262	
	2	23094	10029	9867	
	3	20210	10194	10374	
	4	24409	32998	11899	
	mean	**22370**	**15842**	**10850**	
	stdev	**1799**	**11437**	**906**	
3171PB	1	493	710	1236	
	2	455	693	2132	
	3	704	724	2376	
	4	712	723	2415	
	mean	**591**	**712**	**2039**	
	stdev	**136**	**14.3**	**550**	
3587TS	1	2233	673	1482	
	2	1570	691	1474	
	3	1945	707		
	4	1676	699	1514	
	mean	**1856**	**692**	**1490**	
	stdev	**297**	**14.6**	**21.1**	
3587HS	1	1639	609	1031	
	2	2163	642	1315	
	3	1724	632	1308	
	4	1140	630		
	mean	**1667**	**628**	**1218**	
	stdev	**419**	**13.9**	**162**	
3590TS	1	1124	501	1098	
	2	893	518	1110	
	3	1360	497	1058	
	4	1620	509	1026	
	mean	**1249**	**506**	**1073**	
	stdev	**312**	**9.2**	**38.3**	
PVC-L	1	1741	944	1388	1498
	2	1621	980	1608	
	3	1769	953	1535	
	4	1569	901	1533	
	5	1685	921	1588	
	mean	**1677.0**	**939.8**	**1530**	
	stdev	**82.8**	**30.3**	**86.1**	
PVC-H	1	6024	3538	4792	5195
	2	5919	3490	5237	
	3	5828	3588	4780	
	4	5859	3569	4907	
	5	6158	3591	4896	
	mean	**5958**	**3555**	**4922**	
	stdev	**135**	**42.1**	**185**	

4.4 Cadmium (Cd)

Table 10 compares results for Cd concentration obtained using the HDXRF, HHXRF, and ICP on the sample and reference materials. The certified or expected values noted on certificates are also displayed. At least four measurements were obtained on different locations on materials. The mean and stdev are included in the tables. Figure 11 shows the correlation between the mean Cd concentration measurements obtained by ICP and HDXRF on samples with Cd >5ppm by ICP. Figure 12 shows the correlation between the mean Cd concentration measurements obtained by ICP and HHXRF on samples with Cd >5 ppm by ICP.

The HDXRF Cd measurement results generally compare favorably with the ICP Cd results obtained for the samples. The HDXRF Cd measurement results obtained on the sample materials with ICP Cd results >10 ppm are within ±30% of ICP measurement results. The HHXRF Cd measurement results for many of the PVC sample materials are more than 30 percent lower than the ICP Cd measurement result. The HHXRF Cd measurement result for the PVC-L sample material was only about 10 percent of the ICP Cd measurement result, while the HHXRF and ICP Cd measurement results for PVC-0.01-N2 were within ±15%. Review of the HHXRF spectra for PVC-L and PVC-0.01-N2, which have similar Cd ICP measurement results, showed the intensity of the Cd Kα line to be similar. The PVC-L sample does contain approximately 1000 ppm tin (“Sn”). It may be that the algorithms used by the HHXRF are not correctly accounting for the Sn. The HHXRF spectra for these two sample materials are shown in Figures 13-15. The Cd Kα line is at 23.17 Kev

Figure 11

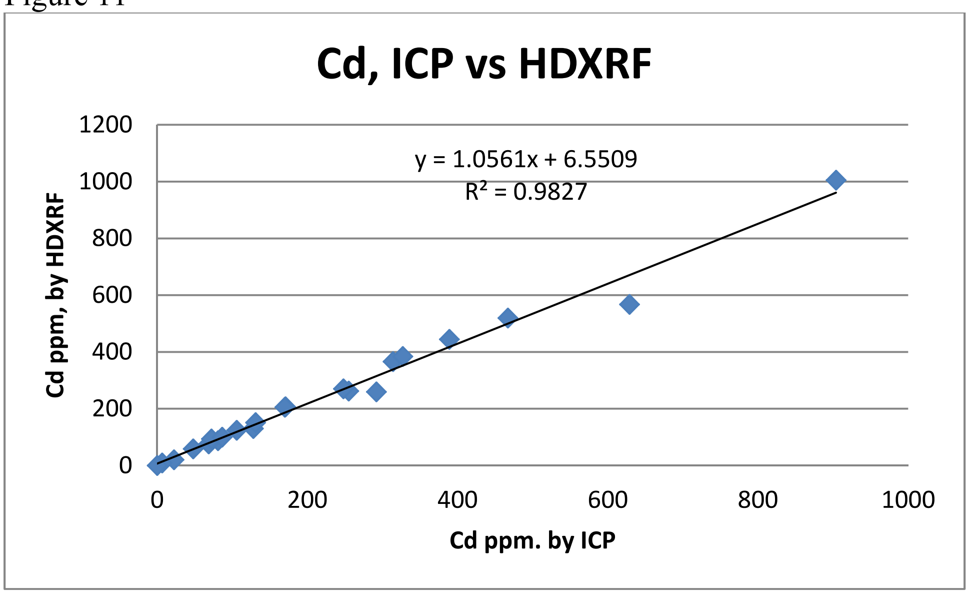

Figure 12

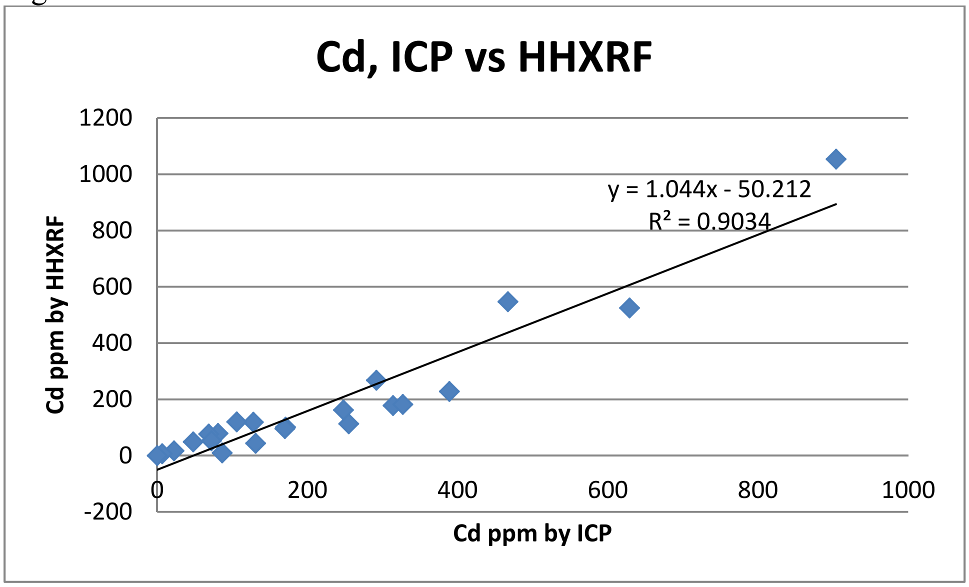

Figure 13. HHXRF spectra of PVC-L sample

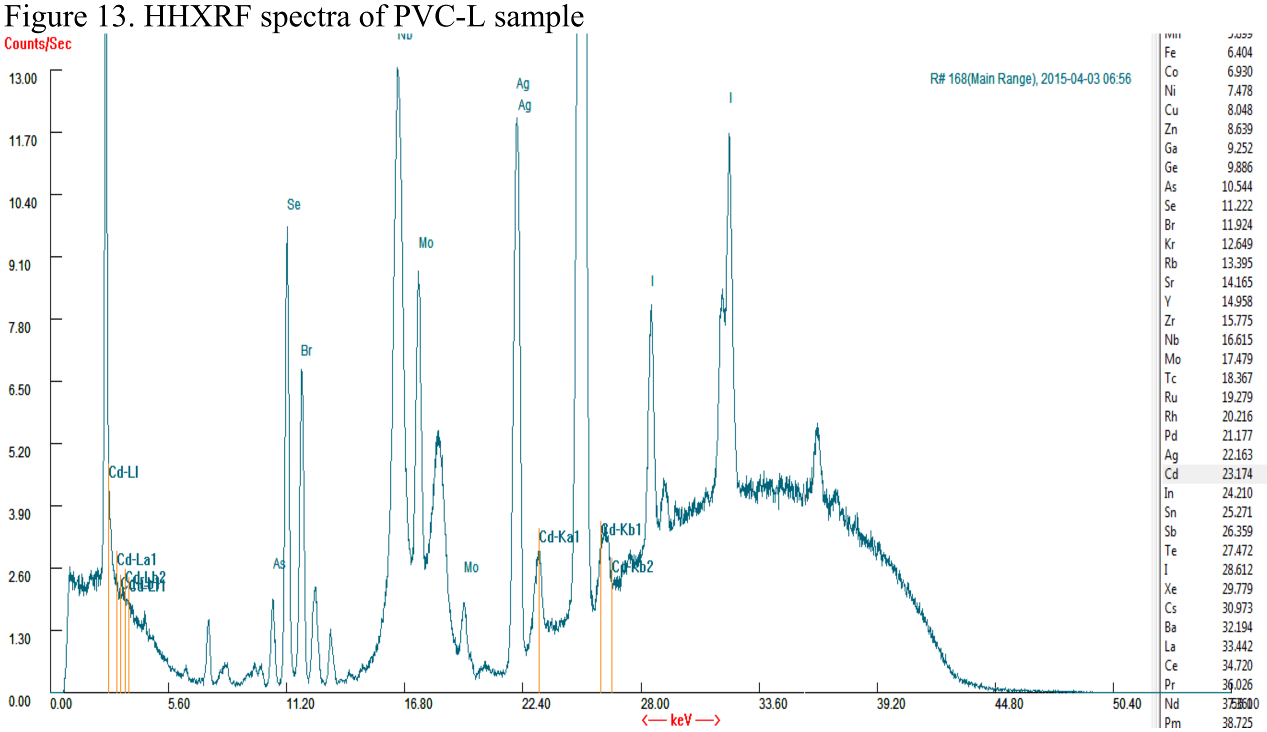

Figure 14. HHXRF spectra of PVC-0.01-N2

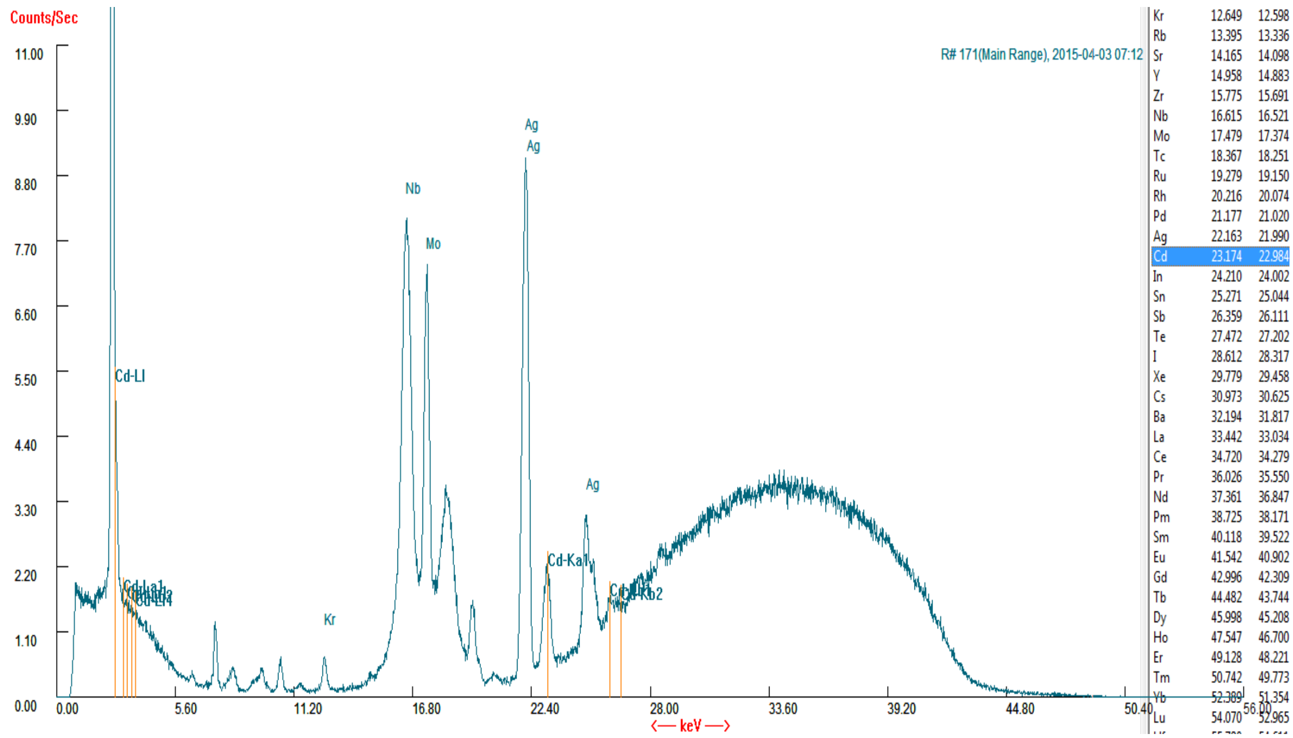

Figure 15. Comparison of PVC-L and PVC-0.01-N2 HHXRF spectra

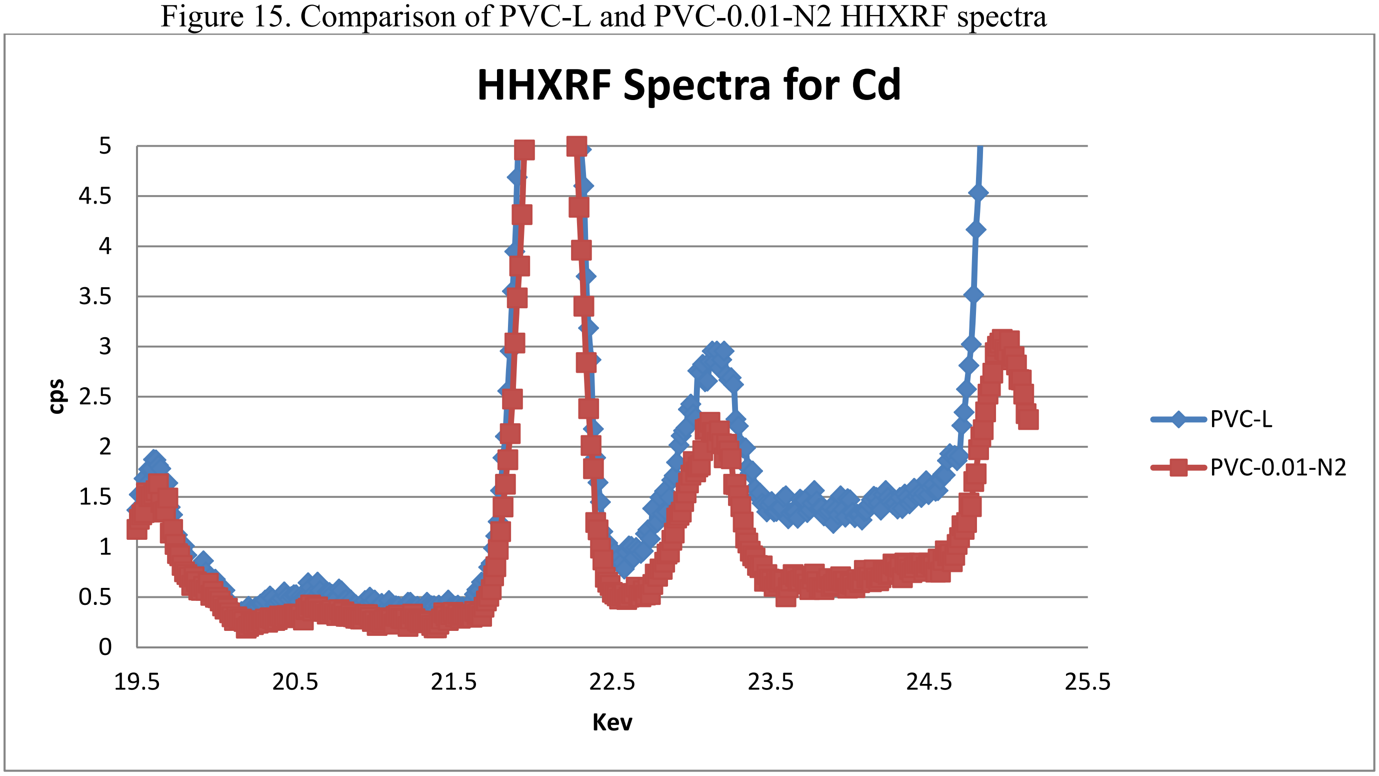

Table 10. Analysis of Materials for Cd

Sample ID	Replicate	HDXRF Cd mg/kg	HHXRF Cd mg/kg	ICP Cd mg/kg	Certified or Added amount of Cd mg/kg
680k	1	18.7	16.2	22.5	**19.6**
	2	18.7	15.6	22.3	
	3	18.3	19.4	22.6	
	4	25.4	17.2	21.7	
	mean	**20.3**	**17.1**	**22.3**	
	stdev	**3.4**	**1.7**	**0.4**	
681k	1	133	120	132	**137**
	2	131	119	126	
	3	123	118	128	
	4	133	117	127	
	mean	**130**	**119**	**128**	
	stdev	**4.8**	**1.3**	**2.6**	
GBW08404	1	9.0	7.3	7.2	**9.2**
	2	8.7	6.3	6.4	
	3	9.2	6.8	6.6	
	4	7.2	7.4	6.5	
	mean	**8.5**	**7.0**	**6.7**	
	stdev	**0.9**	**0.5**	**0.4**	
GBW08405	1	84.1	78.0	82.2	**92.3**
	2	87.9	80.1	83.1	
	3	86.2	78.9	75.1	
	4	91.4	78.5	83.7	
	mean	**87.4**	**78.9**	**81.0**	
	stdev	**3.1**	**0.9**	**4.0**	
EN-71-3	1	283	270	310	**300**
	2	278	269	289	
	3	219	269	235	
	4	257	263	292	
	mean	**259**	**268**	**282**	
	stdev	**29**	**3.3**	**32.5**	
RC1	**mean**	6.0	ND	ND	
4106R	1	566	533	606	
	2	603	521	640	
	3	554	524	602	
	4	545	522	667	
	mean	**567**	**525**	**629**	
	stdev	**25.5**	**5.7**	**30.6**	

Note: ASTM F963-11 Cd total element screening limit is 75ppm

Table 10 Continued. Analysis of Materials for Cd

Sample ID	Replicate	HDXRF Cd mg/kg	HHXRF Cd mg/kg	ICP Cd mg/kg	Certified or Added amount of Cd mg/kg
4960BP	**mean**	ND	ND	ND	
4961GB	1	71.1	78.0	67.4	
	2	77.6	72.0	68.5	
	3	74.8	78.0	70.3	
	4	79.1	80.0	68.8	
	mean	**75.7**	**77.0**	**68.7**	
	stdev	**3.5**	**3.5**	**1.2**	
4960M	**mean**	3.9	ND	ND	
2946T	**mean**	1.8	10.8	ND	
6952BP	**mean**	ND	ND	0.6	
4643C	**mean**	5.3	3.5	2.7	
2946W	**mean**	5.5	ND	0.6	
2949W	**mean**	6.8	ND	ND	
2949H	**mean**	7.0	ND	ND	
3171PB	1	248	111		
	2	244	116	242	
	3	270	113	266	
	4	259	110	278	
	mean	**255**	**113**	**262**	
	stdev	**11.7**	**2.7**	**18.3**	
3588TS	1	213	88.3	168	
	2	197	93.0	167	
	3	202	94.3	176	
	4	217	129	173	
	mean	**207**	**101**	**171**	
	stdev	**9.3**	**18.9**	**4.3**	
3588HS	1	207	84.4	171	
	2	205	122	171	
	3	198	88.8	169	
	4	209	88.9	168	
	mean	**205**	96.1	**170**	
	stdev	**4.8**	**17.6**	**1.4**	
3587TS	1	446	222	374	
	2	458	230	398	
	3	442	230		
	4	431	230	396	
	mean	**444**	**228**	**389**	
	stdev	**11.1**	**4.0**	**13.3**	

Table 10 Continued. Analysis of Materials for Cd

Sample ID	Replicate	HDXRF Cd mg/kg	HHXRF Cd mg/kg	ICP Cd mg/kg	Certified or Added amount of Cd mg/kg
3590B	1	98.1	53.0	72.5	
	2	89.9	52.5	75.5	
	3	93	50.5	71.1	
	4	93.4	55.3	70.0	
	mean	**93.6**	**52.8**	**72.3**	
	stdev	**3.4**	**2.0**	**2.4**	
3590HS	1	149	35.9	130	
	2	155	44.2	130	
	3	158	49.4	132	
	4	141	45.4	133	
	mean	**151**	**43.7**	**131**	
	stdev	**7.5**	**5.7**	**1.9**	
3590TS	1	392	179	340	
	2	384	187	344	
	3	386	179	326	
	4	375	183	298	
	mean	**384**	**182**	**327**	
	stdev	**7.0**	**4.0**	**20.8**	
PVC-L	1	105	7	85.5	**92.8**
	2	102	7	87.5	
	3	101	7	87.0	
	4	96.8	14	87.3	
	5	97.8	13	85.3	
	mean	**99.4**	**9.6**	**86.5**	
	stdev	**2.5**	**3.6**	**0.3**	
PVC-H	1	278	159	256	**278**
	2	283	163	246	
	3	269	163	245	
	4	269	162	243	
	5	261	164	250	
	mean	**270**	**162**	**248**	
	stdev	**9.1**	**1.9**	**2.2**	
3587HS	1	375	180	318	
	2	366	174	315	
	3	367	184	311	
	4	355	176		
	mean	**366**	**178**	**314**	
	stdev	**8**	**4.1**	**3.7**	

Table 10 Continued. Analysis of Materials for Cd

Sample ID	Replicate	HDXRF Cd mg/kg	HHXRF Cd mg/kg	ICP Cd mg/kg	Certified or Added amount of Cd mg/kg
PVC-.005-N2	1	58.1	48	47	**50**
	2	56.8	51	49	
	3	64.2	49	48	
	4	53.7	48	48	
	mean	**58.2**	**49.0**	**47.9**	
	stdev	**4.4**	**1.4**	**0.49**	
PVC-0.01-N2	1	132	119	107	**100**
	2	113	116	106	
	3	130	119	106	
	4	123	126	107	
	mean	**124**	**120**	**106**	
	stdev	**8.6**	**4.2**	**0.51**	
PVC-0.05-N2	1	523	530	465	**500**
	2	516	543	464	
	3	528	578	472	
	4	509	538	467	
	mean	**519**	**547**	**467**	
	stdev	**8.3**	**21.2**	**3.6**	
PVC-0.1-N2	1	980	1039	886	**1000**
	2	1009	1068	892	
	3	1018	1067	948	
	4	1012	1042	889	
	mean	**1005**	**1054.0**	**904**	
	stdev	**16.9**	**15.6**	**29.8**	

4.5 Chromium (Cr)

Some Cr compounds, such as Cr_2O_3, are difficult to dissolve in acids and require the use of perchloric acid ($HCLO_4$) to dissolve. This was reported[5] for the 680k and 681k reference materials used in this study. The plastic materials evaluated in this study were not digested in $HCLO_4$, and incomplete recoveries for Cr were noted in the ICP results of many of the samples. Table 11 compares results for Cr concentration obtained using the HDXRF and HHXRF on the sample and reference materials. ICP results for Cr were not included, due to incomplete digestion of Cr in many of the materials. The certified or expected values noted on certificates are displayed. At least four measurements were obtained on different

[5] Certification Report, The certification of the mass fraction of As, Br, Cd, Cl, Cr, Hg, Pb, S, and Sb and the assignment of indicative values for Sn and Zn in two polyethylene reference materials, Certified Reference Materials ERM®-EC680k and ERM®-EC681k, T. Linsinger, A. Liebich, E. Przyk, A. Lamberty, EUR Report 22784 EN.

locations on materials. The mean and stdev are included in the tables. Figure 16 shows the correlation between the mean Cr concentration measurements obtained by HDXRF and the referenced amounts of Cr reported for reference materials. Figure 17 shows the correlation between the mean Cr concentration measurements obtained by HHXRF and the referenced amounts of Cr reported for the reference materials.

The HDXRF and HHXRF Cr measurement results generally compare favorably with the certified or added amount of Cr reported for the reference materials. Comparisons with ICP could not be made due to incomplete digestion of Cr in many of the plastic materials. The HDXRF and HHXRF Cr measurement results obtained on the reference materials are within ±30% of the certified or added amount of Cr reported for the reference materials, except for 680k, which had Cr HHXRF result approximately 50 percent higher than the certified result. This material only contained 20 ppm Cr, which may be approaching the detection limit of the HHXRF for Cr.

ASTM F963-11 maximum soluble limit for Cr is 60 ppm. If a material screens higher than 60 ppm total Cr, the extraction test is required. The HDXRF and HHXRF successfully identified all the reference materials that had Cr above 60 ppm.

Figure 16

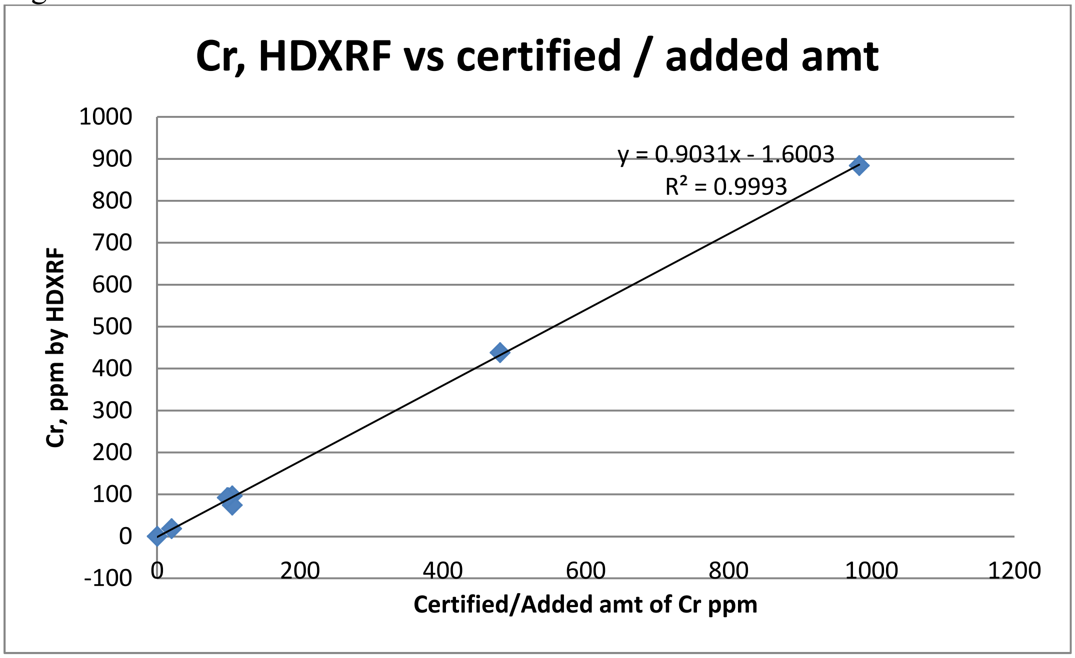

Figure 17

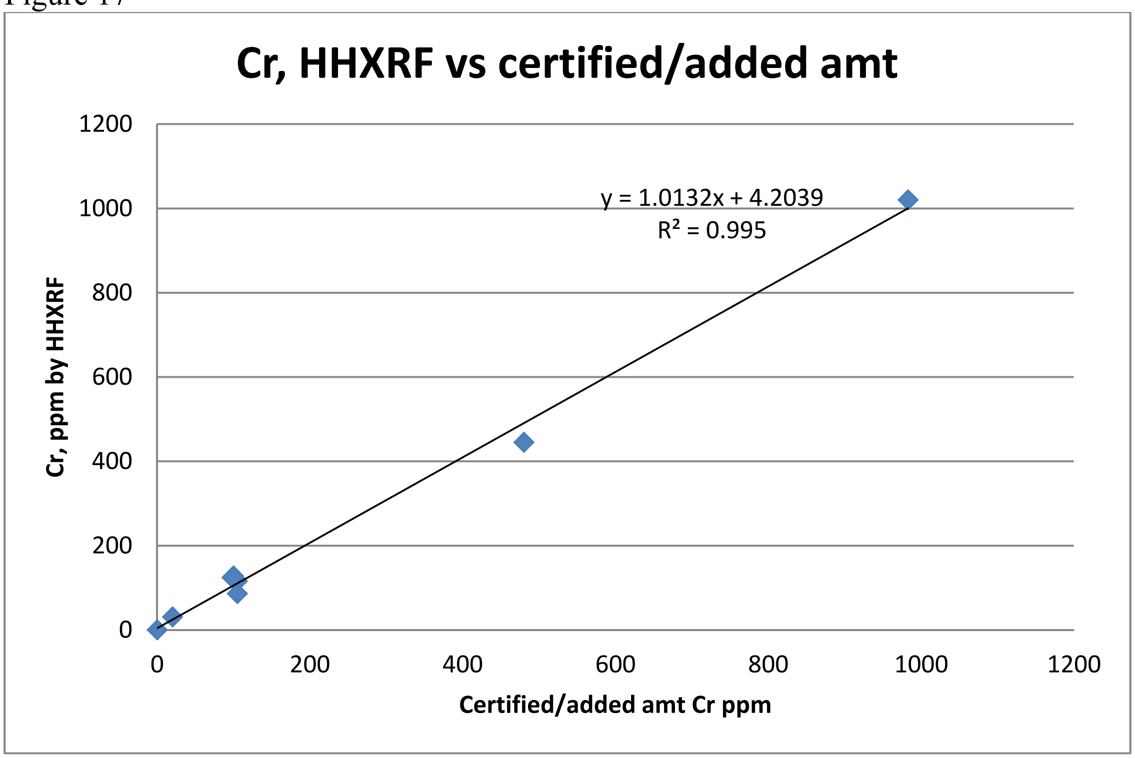

Table 11. Analysis of Materials for Cr

Sample ID	Replicate	HDXRF Cr mg/kg	HHXRF Cr mg/kg	ICP Cr mg/kg	Certified or Added amount of Cr mg/kg
680k	1	19.9	31.9		**20.2**
	2	18.5	30.8		
	3	16.0	31.4		
	4	19.2	28.6		
	mean	**18.4**	**30.7**		
	stdev	**1.7**	**1.5**		
681k	1	95.5	126		**100**
	2	87.6	127		
	3	91.0	128		
	4	93.3	129		
	mean	**91.9**	**128**		
	stdev	**3.4**	**1.1**		
GBW08404	1	86.8	125		**98.1**
	2	89.7	123		
	3	99.1	123		
	4	93.2	124		
	mean	**92.2**	**124**		
	stdev	**5.3**	**0.8**		
GBW08405	1	906	1021		**983**
	2	864	1024		
	3	889	1018		
	4	879	1018		
	mean	**884**	**1020**		
	stdev	**17.6**	**3.2**		
EN-71-3	1	96.3	114		**105**
	2	96.4	114		
	3	97.4	117		
	4	95.1	117		
	mean	**96.3**	**116**		
	stdev	**0.9**	**1.5**		
RC1	1	61.4	199		
	2	59.6	188		
	3	59.6	203		
	4	56.4	205		
	mean	**59.3**	**199**		
	stdev	**2.1**	**7.5**		
4106R	**mean**	ND	ND		
4960BP	**mean**	ND	ND		
4961GB	**mean**	ND	ND		

Note: ASTM F963-11 Cr total element screening limit is 60ppm

Table 11 Continued. Analysis of Materials for Cr

Sample ID	Replicate	HDXRF Cr mg/kg	HHXRF Cr mg/kg	ICP Cr mg/kg	Certified or Added amount of Cr mg/kg
4960M	**mean**	ND	ND		
2946T	**mean**	ND	ND		
6952BP	**mean**	4.4	ND		
4643C	**mean**	ND	ND		
2946W	1	55.9	ND		
	2	51.8	ND		
	3	117	ND		
	4	96.5	ND		
	mean	**80.3**	**ND**		
	stdev	**31.7**			
2949W	**mean**	ND	ND		
2949H	**mean**	ND	ND		
3171PB	**mean**	ND	ND		
3588TS	**mean**	ND	ND		
3588HS	**mean**	ND	ND		
3587TS	**mean**	ND	ND		
3590B	1	61.3	28.3		
	2	49.5	ND		
	3	67.1	ND		
	4	68.1	ND		
	mean	**61.5**	**7.1**		
	stdev	**8.5**	**14.2**		
3590HS	**mean**	ND	ND		
3590TS	**mean**	ND	ND		
3587HS	**mean**	ND	ND		
PVC-L	1	76.3	89		**105**
	2	82.8	85		
	3	83.2	91		
	4	62.1	84		
	5	68.1	82		
	mean	**74.5**	**86.2**		
	stdev	**9.3**	**3.7**		
PVC-H	1	471	437		**480**
	2	431	441		
	3	408	442		
	4	434	454		
	5	445	453		
	mean	**438**	**445**		
	stdev	**22.9**	**7.6**		

4.6 Mercury (Hg)

Table 12 compares results for Hg concentration obtained using the HDXRF, HHXRF, and ICP on the sample and reference materials. The certified or expected values noted on certificates are also displayed. The only materials that had measureable Hg results by HDXRF and HHXRF were the reference materials with intentionally added Hg. Hg analysis by ICP requires additional steps to ensure there is no carryover of Hg between samples. Because Hg was only detected in the reference materials by the XRF analyses, ICP analysis was not conducted on any of the materials. At least four measurements were obtained on different locations on materials. The mean and stdev are included in the tables. Figure 18 shows the correlation between the mean Hg concentration measurements obtained by HDXRF and the referenced amount of Hg reported for the reference materials. Figure 19 shows the correlation between the mean Hg concentration measurements obtained by HHXRF and the referenced amount of Hg reported for the reference materials.

The HDXRF and HHXRF Hg measurement results generally compare favorably with the certified or added amount of Hg reported for the reference materials. The HDXRF and HHXRF Hg measurement results obtained on the reference materials are within ±30% of the certified or added amount of Hg reported for the reference materials except for 681k which had Hg HHXRF and HDXRF results approximately 40 percent higher than the certified result. This material only contained 23.7 ppm Hg.

ASTM F963-11 maximum soluble limit for Hg is 60 ppm. If a material screens higher than 60 ppm total Hg, the extraction test is required. The HDXRF and HHXRF successfully identified all the reference materials that had Hg above 60 ppm.

Figure 18

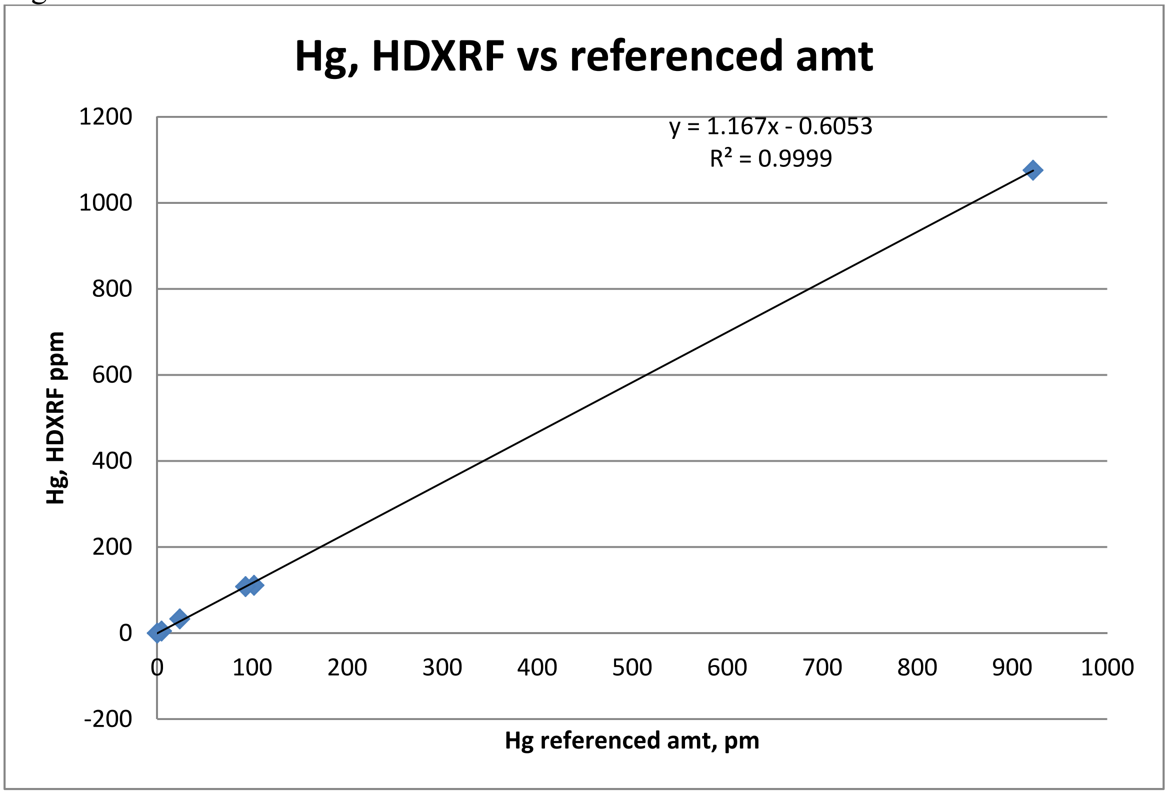

Figure 19

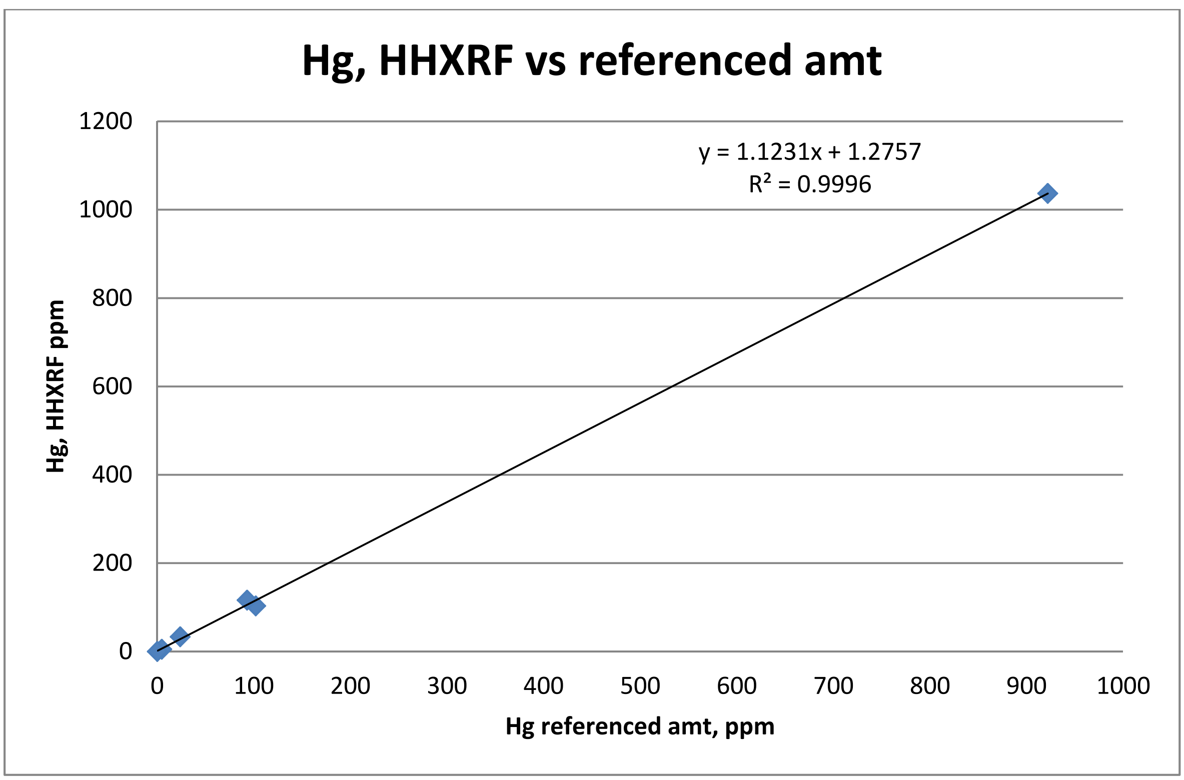

Table 12. Analysis of Materials for Hg

Sample ID	Replicate	HDXRF Hg mg/kg	HHXRF Hg mg/kg	ICP Hg mg/kg	Certified or Added amount of Hg mg/kg
4960M	**mean**	ND	ND		
2946T	**mean**	ND	ND		
6952BP	**mean**	ND	ND		
4643C	**mean**	ND	ND		
2946W	**mean**	ND	ND		
2949W	**mean**	ND	ND		
2949H	**mean**	ND	ND		
3171PB	**mean**	ND	ND		
3588TS	**mean**	ND	ND		
3588HS	**mean**	ND	ND		
3587TS	**mean**	ND	ND		
3590B	**mean**	ND	ND		
3590HS	**mean**	ND	ND		
3590TS	**mean**	ND	ND		
3587HS	**mean**	ND	ND		
RC1	**mean**	ND	ND		
4106R	**mean**	ND	ND		
4960BP	**mean**	ND	ND		
4961GB	**mean**	ND	ND		

Note: ASTM F963-11 Hg total element screening limit is 60ppm

Table 12 Continued. Analysis of Materials for Hg

Sample ID	Replicate	HDXRF Hg mg/kg	HHXRF Hg mg/kg	ICP Hg mg/kg	Certified or Added amount of Hg mg/kg
680k	1	4.9	5.4		**4.64**
	2	6.1	5.8		
	3	3.8	4.1		
	4	4.2	4.5		
	mean	**4.8**	**4.9**		
	stdev	**1.0**	**0.8**		
681k	1	32.9	34.2		**23.7**
	2	32.3	32.7		
	3	34.1	32.5		
	4	33.2	32.7		
	mean	**33.1**	**33.0**		
	stdev	**0.8**	**0.8**		
GBW08404	1	111	116		**93.0**
	2	107	115		
	3	108	114		
	4	105	117		
	mean	**108**	**116**		
	stdev	**2.5**	**1**		
GBW08405	1	1076	1027		**922**
	2	1060	1036		
	3	1076	1030		
	4	1091	1043		
	mean	**1076**	**1037**		
	stdev	**12.7**	**7.1**		
EN-71-3	1	118	103		**102**
	2	116	104		
	3	98.3	103		
	4	113	101		
	mean	**111**	**103**		
	stdev	**8.9**	**1.2**		

4.7 Selenium (Se)

Table 13 compares results for Se concentration obtained using the HDXRF, HHXRF, and ICP on the sample and reference materials. The certified or expected values noted on certificates are also displayed. There were only four materials that had measureable Se results. At least four measurements were obtained on different locations on materials. The mean and stdev are included in the tables. Figure 20 shows the correlation between the mean Se concentration measurements obtained by ICP and HDXRF. Figure 21 shows the correlation between the mean Se concentration measurements obtained by ICP and HHXRF.

The HDXRF Se measurement results compare favorably with the Se ICP measurement result, and are within ±30% of ICP results. Sample 4106R had ICP Se result of 85 ppm, but had ND <111ppm reading by HHXRF. The HHXRF spectrum for 4106R is shown in figure 22, and a peak at the Se Kα line of 11.22Kev is clearly present. The HHXRF measurement results for PVC-L and PVC-H were >60% higher than the ICP measurement results.

ASTM F963-11 maximum soluble limit for Se is 500 ppm. If a material screens higher than 500 ppm total Se, the extraction test is required. The HDXRF and HHXRF successfully identified the two materials that had Se above 500 ppm.

Figure 20

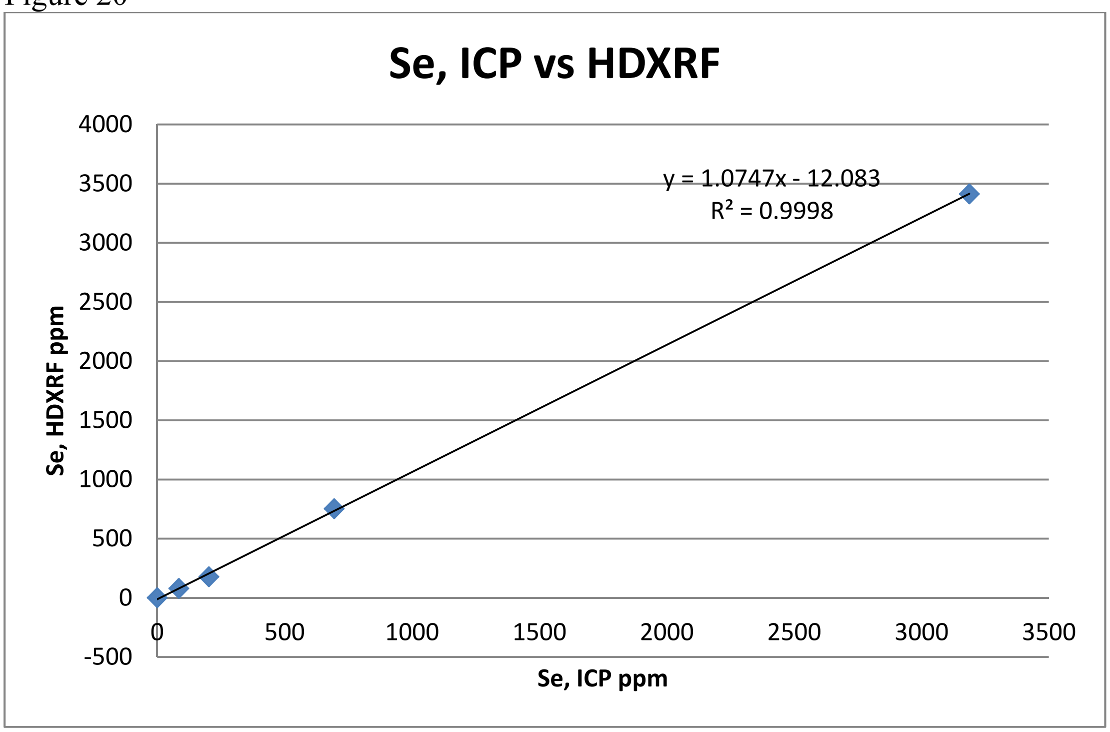

Figure 21

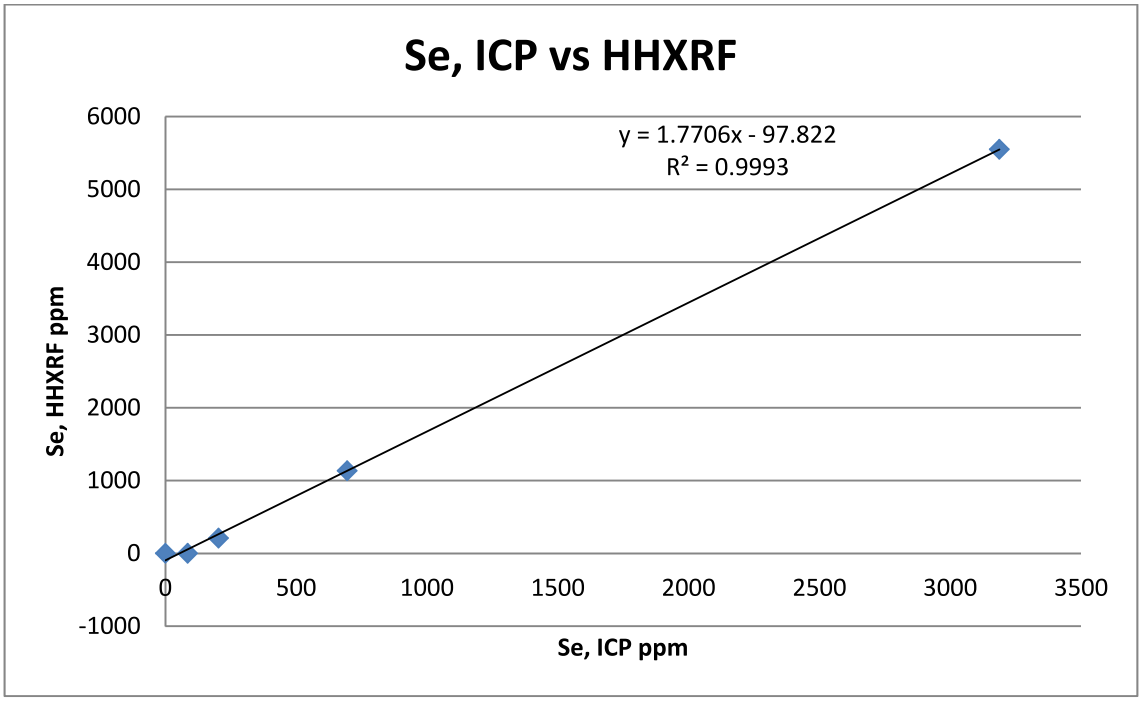

Figure 22 HHXRF spectra of 4106R

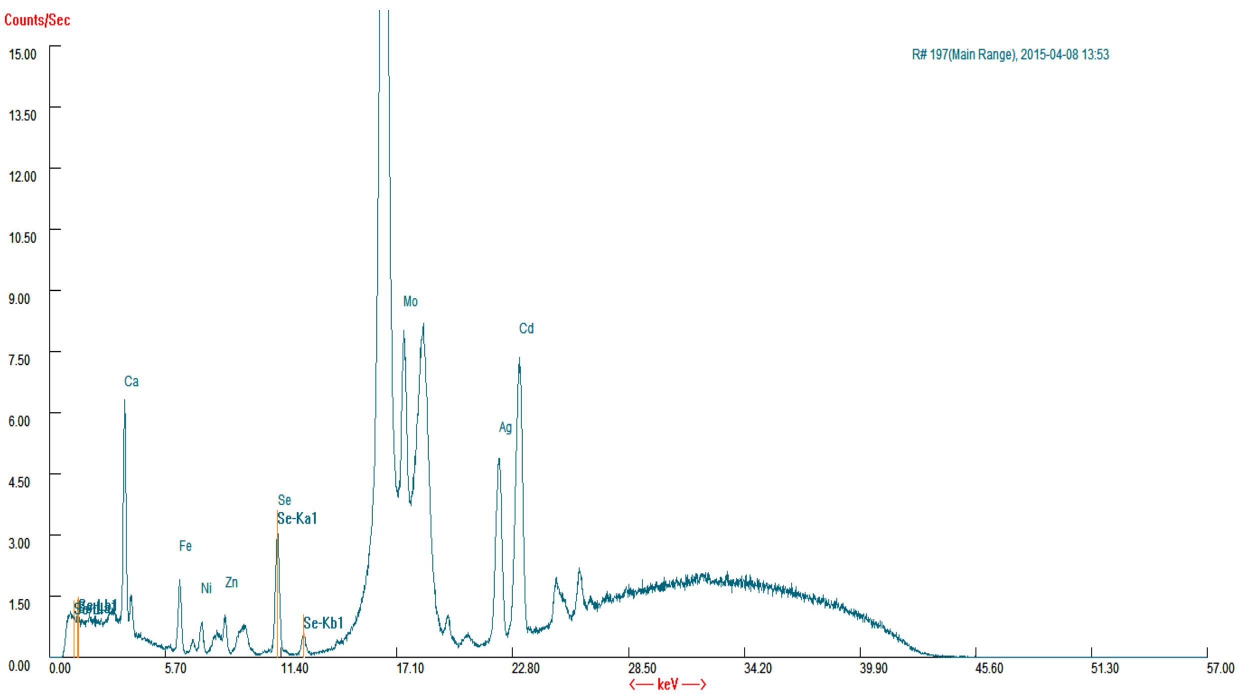

Table 13. Analysis of Materials for Se

Sample ID	Replicate	HDXRF Se mg/kg	HHXRF Se mg/kg	ICP Se mg/kg	Certified or Added amount of Se mg/kg
680k	**mean**	ND	ND	ND	
681k	**mean**	1.1	ND	1.1	
GBW08404	**mean**	ND	ND	6.7	
GBW08405	**mean**	ND	ND	ND	
EN-71-3	1	174	211	223	**203**
	2	193	209	213	
	3	147	210	168	
	4	196	210	206	
	mean	**178**	**210**	**203**	
	stdev	**22.5**	**0.8**	**24.1**	
4106R	1	78.7	ND	82.8	
	2	87.3	ND	87.0	
	3	71.9	ND	78.5	
	4	79.3	ND	91.6	
	mean	**79.3**	**ND**	**85.0**	
	stdev	**6.3**		**5.6**	
RC1	**mean**	ND	ND	ND	
4960BP	**mean**	ND	ND	6.4	
4961GB	**mean**	ND	ND	ND	
4960M	**mean**	ND	ND	6.9	
2946T	**mean**	ND	ND	ND	
6952BP	**mean**	ND	ND	7.1	
4643C	**mean**	ND	ND	5.5	
2946W	**mean**	ND	ND	6.4	
2949W	**mean**	ND	ND	ND	
2949H	**mean**	ND	ND	ND	
3171PB	**mean**	ND	ND	7.4	
3588TS	**mean**	ND	ND	ND	
3588HS	**mean**	ND	ND	ND	
3587TS	**mean**	ND	ND	ND	
3590B	**mean**	ND	ND	6.6	
3590HS	**mean**	ND	ND	7.5	
3590TS	**mean**	ND	ND	ND	
3587HS	**mean**	ND	ND	ND	

Note: ASTM F963-11 Se total element screening limit is 500ppm

Table 13 Continued. Analysis of Materials for Se

Sample ID	Replicate	HDXRF Se mg/kg	HHXRF Se mg/kg	ICP Se mg/kg	Certified or Added amount of Se mg/kg
PVC-L	1	732	1149	727.3	**752**
	2	765	1121	713.0	
	3	737	1117	679.9	
	4	747	1137	659.8	
	5	783	1153	696.3	
	mean	**753**	**1135.4**	**695.3**	
	stdev	**21.1**	**16.1**	**26.6**	
PVC-H	1	3300	5548	3244	**3665**
	2	3245	5546	3102	
	3	3774	5621	3205	
	4	3342	5200	3103	
	5	3399	5839	3287	
	mean	**3412.0**	**5550.8**	**3188**	
	stdev	**210.1**	**229.7**	**83.4**	

5.0 CONCLUSIONS AND RECOMENDATIONS

CPSC staff notes that the *Soluble Element Test Method for Substrate Material* described in part 8.3.5 of ASTM F963-11 test is for solubility. Staff's experience is that typically well below 100 percent of any of these elements that might be present in a polymeric material would be soluble in the conditions of the ASTM F963-11 test. Thus, there is an added "safety factor" present in allowing the use of HDXRF for total element screening because even if slightly higher elemental content is present in the material than the XRF detected, this would be compensated by the knowledge that well below 100 percent of the element would be extracted from the polymeric material following the soluble element test method.

5.1 HDXRF

HDXRF technology is suitable in many cases for the accurate determination of lead and other elements in homogeneous polymeric materials. A standard test method, ASTM 2853-10e1, is available. The data provided in this report demonstrate that HDXRF is a suitable alternative test method for measuring total content of heavy metals in homogeneous polymeric materials. The method shows a similar level of accuracy and repeatability as traditional wet chemistry. It is recommended that this test method be accepted as an approved alternative total screening test method in the ASTM F963-11 standard.

5.2 HHXRF

HHXRF technology has the potential to be a suitable alternative test method for measuring total content of heavy metals in homogeneous polymeric materials. Based on the results, it appears that the HHXRF instrument used in this study is capable of detecting Sb, As, Ba, Cd, Cr, Hg, and Se below the ASTM F963-11 total element screening thresholds. The following discrepancies are noted in the comparisons of HHXRF measurement results and the ICP measurement results or referenced amounts:

a. HHXRF Sb results for the PVC-L, PVC-H, and several other PVC samples that were about 30 percent lower than the ICP measurement result.
b. HHXRF was unable to detect As in some sample materials that had ICP and HDXRF measurement results just below the 25 ppm As screening threshold. The HHXRF measurement result for 4960B sample was about 60 percent lower than the ICP and HDXRF measurement results. The mean ICP As result for 4960B was 27 ppm just over the 25 ppm limit. The mean HHXRF result for 4960B was 10 ppm.
c. HHXRF Cd results for the PVC-L, PVC-H and several other PVC samples were more than 30 percent lower than the ICP measurement result. The presence of Sn in these samples may not have been properly accounted for in the HHXRF solver algorithms used for PVC materials.
d. HHXRF Se results for the PVC-L and PVC-H samples were about 60 percent higher than the ICP and HDXRF measurement results.

Standard test methods using HHXRF with scopes that cover the ASTM F963-11 extractable limits for Sb, As, Ba, Cd, Cr, Hg, and Se are not currently available. There is also a lack of PVC and olefin polymeric certified reference materials containing Sb, As, Ba, Cd, Cr, Hg, and Se near the ASTM F963-11 total element screening threshold limits. Development of appropriate certified reference materials could assist HHXRF manufacturers in developing their calibration profiles to more accurately quantify heavy metals in polymeric materials. Staff members from the CPSC are working with the National Institute of Standards and Technology ("NIST") to develop appropriate PVC Standard Reference Materials ("SRMs") containing Sb, As, Ba, Cd, Cr, Hg, and Se.CPSC staff encourages HHXRF manufacturers to develop standard test methods that could be used for ASTM F963-11 total element screening when validated with appropriate certified reference materials. CPSC-CH-E1002-8.3 Standard Operating Procedure for Determining Total Lead (Pb) in Nonmetal Children's Products, Revision November 15, 2012 http://www.cpsc.gov/PageFiles/137832/CPSC-CH-E1002-08_3.pdf. Section I.C Identification and Quantification of Pb in Siliceous Materials Using Other Forms of XRF Spectrometry could be used a guideline. The procedure should utilize appropriate sampling, testing, calibration, and quality control guidelines that would validate the HHXRF instrument is suitable for testing Sb, As, Ba, Cd, Cr, Hg, and Se in polymeric materials in the range of interest, with detection limits below the maximum soluble element limits listed in Table 1 of the ASTM F963-11.

List of Tables, Figures, Abbreviations, and Acronyms

CPSC= U.S Consumer Product Safety Commission
Sb= Antimony
As= Arsenic
Ba= Barium
Cd = Cadmium
Cr= Chromium
Hg= Mercury
Se= Selenium
M=molar
XRF= X-ray Fluorescence Spectrometry
HDXRF= High Definition XRF

List of Tables, Figures, Abbreviations, and Acronyms, Continued

HHXRF= Handheld XRF
ICP=Inductively Coupled Plasma Optical Emission Spectrometry
ICP-MS= Inductively Coupled Plasma Mass Spectrometry
GFAA= Graphite Furnace Atomic Absorption
keV= kilo electron volt
ppm= parts per million
µg/ml= microgram per milliliter
L/min= liters per minute
rpm= rotations per minute
kw= kilowatt
PVC= polyvinyl chloride
FTIR= Fourier Transform Infrared Spectrometry