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Tube-Based Field-Portable X-ray Fluorescence (FPXRF) as a Qualitative Screening Tool for Resource Conservation and Recovery Act (RCRA) Metals in Children's Products and Comparison to Total Metals Analyses to Predict Hazardous Waste Metals Toxicity Characteristic

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Tube-Based Field-Portable X-ray Fluorescence (FPXRF) as a Qualitative Screening Tool for Resource Conservation and Recovery Act (RCRA) Metals in Children's Products and Comparison to Total Metals Analyses to Predict Hazardous Waste Metals Toxicity Characteristic

By: James M. Kohlbach

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Abstract

This research was performed to assess the efficacy of tube-based field portable x-ray fluorescence (FXPXRF) devices to evaluate RCRA heavy metal concentrations in children’s products and determine potential hazardous waste toxicity characteristics by comparative analysis to inductively coupled plasma (ICP) yields per SW6010B. Sample sets consisting of wood, plastic, rubber, bulk, plated/coated, and metal matrices were purchased, size-reduced as necessary and directly analyzed three-times for 120 seconds each via FPXRF operated in the *Consumer Goods/Test All* mode. Subsequently, the same samples were prepared in accordance to SW3050B and analyzed via ICP at an accredited contract laboratory. Side-by-side results analysis indicates that FPXRF consistently exhibits positive bias compared to standard laboratory methods in the majority of matrices due to XRFs abilities to estimate total metallic analyte concentrations versus extract-labile substances only. Instances in which FPXRFs positive bias was absent were believed attributed to suboptimal sample homogeneity or limited sample area compared to total sample volume of SW3050B extraction. Though FPXRFs overestimation of metallic analyte concentrations does not directly correlate to SW6010B ICP yields without application of correction factors, it does provide a better indication of total versus liberated analyte presence.

Keywords: XRF, X-Ray, Heavy Metals, Children’s Products, Screening, RCRA, Hazardous Waste, Recall, Consumer Goods

Introduction

Since promulgation of the Federal Hazardous Substances Act (FHSA) on July 12, 1960[1], American consumers have been afforded governmentally-imposed product protections through compulsory hazard labeling requirements or outright hazardous substance bans. FHSA defines a *hazardous substance* as:

> *Any substance or mixture of substances which (i) is toxic, (ii) is corrosive, (iii) is an irritant, (iv) is a strong sensitizer, (v) is flammable or combustible, or (vi) generates pressure through decomposition, heat or other means, if such substance or mixture of substances may cause substantial personal injury or substantial illness during or as a proximate result of any customary or reasonably foreseeable handling or use, including reasonably foreseeable ingestion by children.*[2]

In accordance with 15 U.S.C § 1261(g), *toxic* is defined as:

> *Any substance (other than a radioactive substance), which has the capacity to produce personal injury or illness to man through ingestion, inhalation or absorption through any body surface*.

Furthermore, the FSHA regulates a *banned hazardous substance* as:

> *Any toy or other article intended for use by children, which is a hazardous substance, or which bears or contains a hazardous substance in such manner as to be susceptible of access by a child to whom such toy or other article is entrusted.*[3]

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[1] 15 U.S.C. § 1261 - 1268

[2] 15 U.S.C. § 1261(f)(1)(A)

[3] 15 U.S.C. § 1261(q)(1)(A)

Provided an underlying toxicity characteristic exists which renders a substance hazardous and that substance is contained in an article or toy intended for use by a child; it is therefore a banned hazardous substance prohibited from introduction, delivery[4] or receipt[5] in interstate commerce. The FHSA empowers the Consumer Products Safety Commission (CPSC), through the Consumer Products Safety Act (CPSA), to oversee bans on certain products which are so dangerous or the nature of the hazard is such that labeling in itself is inadequate for consumer protection.[6]

For forty-eight years, a regulatory infrastructure allowing seizure of misbranded or banned hazardous substances[7] and aimed at consumer protectionism has existed in the U.S. - the efficacy of which remains a contentious subject beyond scope and topic of this research. 'In-scope' however, is the slew of recent children's products recalls due to toxic contaminants and the apparent failure of our regulatory framework to furnish adequate consumer and child protections.

1.1 Focus

This multi-faceted research has sequentially: 1) examined banned hazardous substances in the form of infants/children's products and toys which have infiltrated the United States market; 2) assessed the viability of pre-market product screening utilizing field-portable x-ray fluorescence (FPXRF) technology; 3) evaluated banned children's products against Resource Conservation and Recovery Act (RCRA) heavy metals hazardous waste toxicity characteristics through total metals and toxicity characteristic

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[4] 15 U.S.C § 1263(a)

[5] 15 U.S.C § 1263(c)

[6] Requirements under the Federal Hazardous Substances Act: Labeling and Banning Requirements for Chemicals and Other Hazardous Substances 15 U.S.C §1261 and 16 C.F.R. Part 1500. August 2002 www.cpsc.gov/BUSINFO/regsumfhsa.pdf (Accessed 04/02/08).

[7] 15 U.S.C. § 1265(a)

leaching procedure (TCLP) analysis, and; 4) determined if matrix-specific FPXRF analytical yields may be effective predictors of hazardous waste toxicity characteristics.

1.2 Significance

The research was selected due to its uniqueness and timeliness; however the February 2006 death of Jarnell Brown - a four-year old Minneapolis boy who died from acute lead-poisoning after ingestion of a Chinese-made Reebok "promotion" charm bracelet[8] [Figure 1.0] - functioned as the primary driver. Minneapolis Public Health Department post-autopsy analysis of the ingested charm, in accordance with EPA Method 3050 yielded a 99.1% reported lead content.[9] The situation was addressed through a Reebok-initiated 300,000 unit voluntary recall.

Figure 1.0

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[8] Associated Press, "Environmental Group Sues EPA Over Toy Jewelry Lead", September 14, 2006. http://wcco.com/topstories/toy.jewelry.lead.2.372793.html (Accessed 04/06/08)
[9] http://www.cdc.gov/mmwr/preview/mmwrhtml/mm55d323al.htm (Accessed 04/06/08)

The inaugural CPSC recall for a contaminated toy occurred December 7, 1976 in which 15,000,000 benzene-contaminated Bubo Plastic Bubb-A-Loons were pulled from market.[10] Less than one-year later, 60,000 "Snoopy" Toy Banks were recalled on September 12, 1977 for violation of paint containing lead (Pb) in concentration greater than the 0.5% (5,000 ppm) federal standard.[11] Fast forward thirty-years and 2007 lays witness to 105 infant/children's products and toy recalls[12] for lead[13], kerosene and GHB[14] contamination – the result is 21,372,110 units removed from interstate commerce.[15] Further study, outside the scope of this work, is warranted to evaluate if the increase is attributed to globalization, recycling, consumer-advocacy organization self-policing with FPXRF, limited resources available for imports screening or other unrelated contributory factors.

CPSC currently utilizes two test methodologies, conducted sequentially, for evaluation of lead (Pb) hazards in children's products. First, a sample is "screened" for total lead in accordance with Canada Product Safety Bureau Method C-02.4. If total Pb yield exceeds the 0.06% actionable level, an acid extraction test is performed in accordance with ASTM Methods C927, C738, D5517 and F963 to determine migratory lead bioavailability.[16] Though there are no validity concerns with the preceding methodologies, timeliness, resource intensity, destructive vs. non-destructive nature and resultant waste byproducts are concerns of the author.

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[10] http://www.cpsc.gov/cpscpub/prerel/category/toy.html (Accessed 09/15/08)

[11] http://www.cdc.gov/nceh/lead/recalls/toys.htm (Accessed 04/04/08)

[12] CPSC classifies toys differently from infants/children's products. Toys are self explanatory, whereas the latter may include children's jewelry, stationary, arts, crafts, ornaments and other seasonal items. This research does not address any type of children's apparel recalled for hazardous substances.

[13] 16 C.F.R Part 1303 sets the Federal lead (Pb) standard of 0.06% (600 ppm)

[14] Gammahydroxy butyrate (a.k.a. - gamma hydroxybutyric acid). Commonly referred to as the "date-rape" drug.

[15] Information obtained from spreadsheet created by author, which contains historical CPSC 'toys' and 'infants/children's products' recall data to allow totalizing and graphical representation.

[16] "Standard Operating Procedure for Determining Lead (Pb) and Its Availability in Children's Metal Jewelry". CPSC. February 3, 2005. http://www.cpsc.gov/BUSINFO/pbjeweltest.pdf (Accessed 04/04/08)

Due to refined product demand and technological advancements - mainly spurred by the European Union Restriction of Certain Hazardous Substances Directive 2002/95/EC (RoHS) - the demand for and capabilities of field-portable x-ray fluorescence (FPXRF) equipment continues to evolve and therefore must be given consideration as a potentially viable, in-situ screening assessment tool. In 2006 alone, the global market demand for handheld XRF increased 70%; a phenomenon many believe was directly attributed to EU RoHS.[17] FPXRF allows analytical equipment to be transported to the sample, not vise-versa; thus eliminating rigorous sample collection efforts, chain-of-custody documentation and sample transport. Additionally, XRF analysis is non-destructive; thus a sample that screens positive and requires further analysis may be shipped intact to an analytical laboratory for confirmatory quantification. XRF sample cycle times are matrix dependent and usually fall within the 30 – 300 seconds range, therefore supporting large sample-set analytical turnarounds on a daily basis. Furthermore, FPXRF does not require "wet-lab" infrastructure and highly-trained analytical chemists, nor does it result in potentially hazardous waste by-products.

Prior research addressing FPXRF metals screening capabilities for alloy confirmation, for lead paint determination, for false-jewelry investigation, for metals in soil, mulch and pressure-treated wood and even leaded-gasoline in foreign countries has been performed.[18,19] In contrast, a paucity of published work exists assessing tube-based FPXRFs application in the screening of infants/children's products and toys - and to date,

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[17] http://spectroscopymag.findpharma.com/spectroscopy/Market+Profile+Column/Market-Profile-Handheld-XRF/ArticleStandard/Article/detail/406625 (accessed 11/11/08)

[18] A.K Khusainov and others, "Portable and X-ray analyzers based on CdTe p-i-n detectors", *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment,* 428, no. 1 (1999). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 01/03/08).

[19] Colleen N. Block, Tomoyuki Shibata and Helena Solo-Gabriele, "Use of handheld X-ray fluorescence spectrometry units for identification of arsenic in treated wood", *Environmental Pollution*, 148, no.2 (2007). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 01/03/08).

the author was unable to locate viable literature regarding FPXRF metals yields as effective predictors of RCRA heavy-metals toxicity characteristic(s).

The work illustrates that FPXRF has been successfully utilized and deemed a viable screening tool in many industrial, remedial and toxicological applications and could likely realize the same successes in children's products screening. In-situ, real-time analytical capabilities would allow for increased product sampling densities at overall lower costs and prevent discrepant product from actually entering interstate commerce. Provided correlation is established between FPXRF and TCLP analyses of differing matrices, it is logical to surmise that initial FPXRF screening data may be utilized to predict RCRA hazardous waste metals-toxicity.

1.3 Purpose

This research, through parallel inquiry, gathered historical and contemporaneous data to perform an objective capabilities assessment regarding FPXRFs viability as a qualitative screening tool for RCRA metals determination in infants/children's products and toys, and attempted to evaluate the correlation between matrix-specific FPXRF metals yields and RCRA hazardous waste metals toxicity.

1.4 Terminology

1.4.1 The following terms and definitions are applicable to this research

1.4.1.1 AAS – Atomic Absorption Spectroscopy

Atomic-absorption (AA) spectroscopy uses the absorption of light to determine the concentration of gas-phase atoms. Liquid or solids samples are vaporized (atomized) in a flame or graphite furnace. The atoms absorb UV or visible light and transition to higher electron energy levels where concentration is determined from the amount of absorption.

1.4.1.2 ASTM - American Society of Testing and Materials

American Society of Testing and Materials is one of the largest voluntary standards development organizations in the world publishing technical standards for materials, products, systems, and services.

1.4.1.3 CPSA - Consumer Product Safety Act

Consumer Product Safety Act enacted in 1972, is CPSC's umbrella statute. It established the agency, defines its authority, and provides that when the CPSC finds an unreasonable risk of injury associated with a consumer product it can develop a standard to reduce or eliminate the risk. The CPSA also provides the authority to ban a product if there is no feasible standard, and it gives CPSC authority to pursue recalls for products that present a substantial product hazard.[20]

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[20] http://www.cpsc.gov/businfo/cpsa.html (Accessed 5/5/08)

1.4.1.4 CPSC – Consumer Product Safety Commission

The U.S. Consumer Product Safety Commission is charged with protecting the public from unreasonable risks of serious injury or death from more than 15,000 types of consumer products.[21]

1.4.1.5 EDXRF – Energy Dispersive X-Ray Fluorescence

Energy Dispersive X-Ray Fluorescence equipment functions on the principle that the pulse height of the detector signal (fluoresced energy) is proportional to the X-ray photon energy. Samples are irradiated by X-rays from a tube or radioisotope and elements and their concentration are identified by counting the pulses at the different energy levels via a multichannel analyzer.[22]

1.4.1.6 FHSA – Federal Hazardous Substances Act

Federal Hazardous Substances Act requires certain hazardous household products to bear cautionary labeling that alerts consumers of the potential hazards those products present and inform of safe-use measures. It also gives the CPSC authority to ban a hazardous substance if the product is deemed so hazardous that the cautionary labeling is inadequate for public protection.[23]

1.4.1.7 FAAS – Flame Atomic Absorption Spectrometry (see "AAS")

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[21] http://www.cpsc.gov/cpscpub/prerel/prerel.html (Accessed 5/5/08)
[22] http://www.panalytical.com/index.cfm?pid=133 (Accessed 5/4/08)
[23] http://www.cpsc.gov/BUSINFO/fhsa.html (Accessed 5/4/08)

1.4.1.8 FPXRF – Field Portable X-Ray Fluorescence

Field Portable X-Ray Fluorescence functions on the same principles as EDXRF and the two terms are often used interchangeably. The key distinction of FPXRF versus standard laboratory equipment is the portability of the former allows in-situ sampling.

1.4.1.9 GC-MS – Gas Chromatography-Mass Spectroscopy

Gas Chromatography-Mass Spectroscopy is the combination of two analytical techniques for a single method of analyzing mixtures of chemicals. GC separates the mixture components and MS characterizes each of them individually.[24]

1.4.1.10 Hazardous Waste

Hazardous waste is a solid waste that is either listed or exhibits a hazardous characteristic as defined per 40 CFR Part 261.

1.4.1.11 ICP-AES-Inductively Coupled Plasma-Atomic Emission Spectroscopy

Inductively Coupled Plasma-Atomic Emission Spectroscopy is based on the principle that excited electrons of different chemical character emit energy at a specific wavelength upon return to ground state. Thus, knowing the intensity of emitted wavelength is proportional to concentration, one can quantify the elemental composition of a sample.

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[24] http://www.gmu.edu/departments/SRIF/tutorial/gcd/gc-ms2.htm (Accessed 5/4/08)

1.4.1.12 Method 1311

Method 1311 is the analytical methodology used for conducting the Toxicity Characteristic Leaching Procedure. (See "TCLP")

1.4.1.13 Method 6200

Method 6200 entitled "Field Portable XRF Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment" is the official EPA methodology for performing FPXRF analysis.

1.4.1.14 NGO

Non-governmental organization is a legally recognized establishment formed by private associations or people and has no participation or representation by any form of government. NGOs may be wholly or partially funded by governments, but maintain their non-governmental status by denying membership to government representatives.

1.4.1.15 RoHS – Restriction of Certain Hazardous Substances

The 2002/95/EC Directive (as amended) stands for "the restriction of the use of certain hazardous substances in electrical and electronic equipment" (EEE) and bans placing new EEE containing greater than maximum concentration values (MCVs) of lead, cadmium, mercury, hexavalent chromium, polybrominated biphenyl (PBB) and polybrominated diphenyl ether (PBDE) flame retardants on the EU market.[25]

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[25] http://eur-lex.europa.eu/pri/en/oj/dat/2003/l_037/l_03720030213en00190023.pdf (Accessed 5/5/08)

1.4.1.16 RCRA – Resource Conservation and Recovery Act

The Resource Conservation and Recovery Act, passed on October 21, 1976 in response to the growing volumes of municipal and industrial wastes, is a public law governing the proper management of solid and hazardous wastes.[26]

1.4.1.17 "RCRA metals"

RCRA metals include Arsenic (As), Barium (Ba), Cadmium (Cd), Chromium (Cr), Lead (Pb), Mercury (Hg), Selenium (Se) and Silver (Ag)

1.4.1.18 SW-846

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, is the USEPA official compendium of analytical and sampling methodologies that have been evaluated and approved for use in complying with the RCRA regulations.[27]

1.4.1.19 TCLP – Toxicity Characteristic Leaching Procedure

The Toxicity Characteristic Leaching Procedure (SW-846 Method 1311) is designed to characterize the mobility (leachability) of organic/inorganic susbtances contained in liquid, solid, and multiphase wastes to determine if the material meets the definition of toxicity and requires assignment of applicable 40 CFR Part 261 EPA RCRA waste codes D004 through D052.

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[26] http://www.epa.gov/osw/laws-reg.htm (Accessed 5/5/08)

[27] http://www.epa.gov/epaoswer/hazwaste/test/sw846.htm (Accessed 5/5/08)

1.4.1.20 Totals analysis

Performed in accordance with SW-846 Method 3050 to determine metal(s) concentration(s) less than or equal to 20 times the TCLP limits. The total metal concentration versus leachable portion is determined.

1.4.1.21 Tube-based

Tube-based means the x-ray is created via an x-ray tube versus a radioactive isotope source.

1.4.1.22 UE/AVS – Ultrasonic Extraction/Anodic Stripping Voltammetry

Ultrasonic Extraction/Anodic Stripping Voltammetry is a high-frequency sample preparation technique followed by electrochemical method for trace analyses of metals. Solubilized metal ions are reduced to metallic form, concentrated as a mercury amalgam in a mercury film electrode and then re-oxidized into solution ("stripped") from the electrode. Metal that remains within the mercury amalgam is then analyzed.[28]

1.5 Research Questions

The questions of primary and secondary research interest were:

1.5.1 Primary

Is tube-based FPXRF a viable and employable technology for RCRA heavy metals screening of infants/children’s products and toys?

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[28] http://www.chem.usu.edu/~sbialkow/Classes/565/ASV.html (Accessed 5/5/08)

1.5.2 Secondary

Is it possible to predict RCRA hazardous waste metal(s) toxicity characteristics from matrix-specific FPXRF yields?

1.6 Deliverable

The key work product of this research was the development of infants/children's products and toys tube-based FPXRF assessment methodologies and corresponding analytical report tables (Tables 5.0 – 6.0) delineating the yields between FPXRF, total metals and toxicity characteristic leaching procedure (TCLP) analyses. However, due to limited sample availability subsequent to total metals analysis on a matrix which satisfied the TCLP evaluation parameters, the laboratory was unable to perform the latter. Therefore, response to the primary research question is "yes, but FPXRF is not the simple point-and-shoot technology which it is touted." Due to sample and corresponding data unavailability, the answer to the second research question is simply, "unknown based on current research".

Background

This work has been segregated into three distinct components; each of which requires dedicated discussion to effectively establish the overall problem statement and reinforce the purpose of this thesis research.

2.1 Children's Products Safety – Federal Legislation

The Federal Hazardous Substances Act and Consumer Product Safety Act are two primary federal statutes tasked with consumer goods protection through mandated product labeling requirements and outright prohibition of certain product entry into interstate commerce. Similar state, county and municipality-level programs have not been addressed in this work as optimally-performing federal requirements should theoretically eliminate need for same-scope downstream legislation.

Codified at 15 U.S.C § 1261 – 1278, the Federal Hazardous Substances Act entered-into-force July 12, 1960 and mandates that hazardous household products display cautionary labeling that alerts consumers to the potential product hazards and delineates proper self-protection measures. Products shall meet the following criteria to require cautionary labeling:

- Classified as either corrosive, toxic, combustible, flammable, irritant, sensitizer or pressure generating via heat, decomposition or other means,

  and;
- May cause substantial personal injury or illness during or resultant of reasonably foreseeable handling or use, including possible ingestion by children.

Under the Act, toys or other articles intended for infants/children's use, which contain accessible hazardous substances, including small parts, or present electrical, mechanical or thermal hazards are banned since cautionary labeling alone does not afford adequate protections.

The Consumer Product Safety Act of 1972, codified at 15 U.S.C. § 2051 – 2084, established the Consumer Product Safety Commission (CPSC) as an independent agency of the United States government. Empowered by the FHSA, the CPSC upholds the right to develop safety standards and activate recalls for over 15,000 consumer products which may present unreasonable risk of injury or death. In product instances where safety standards and precautionary labeling do not offer satisfactory protections, the CPSC reserves the right to ban a product outright[29]. Excluded from FHSA/CPSC jurisdiction, since under purview of other governmental agencies, are food, drugs, tobacco products, pesticides, aircraft, boats, motor vehicles, firearms and ammunition, cosmetics and medical devices.

This portion of research examined the history of CPSC *Product Category* recalls [1976 – 2007], due to *toxic* contaminants for infant/children's products and toy categorical classifications; it does not include apparel within the infant/children's classification or household, outdoor, sports and recreation or specialty products. Appendix A represents a single, comprehensive data file of CPSC toxic recalls evaluable by year, country of manufacture, hazard type, categorical classification or recalled unit volume.

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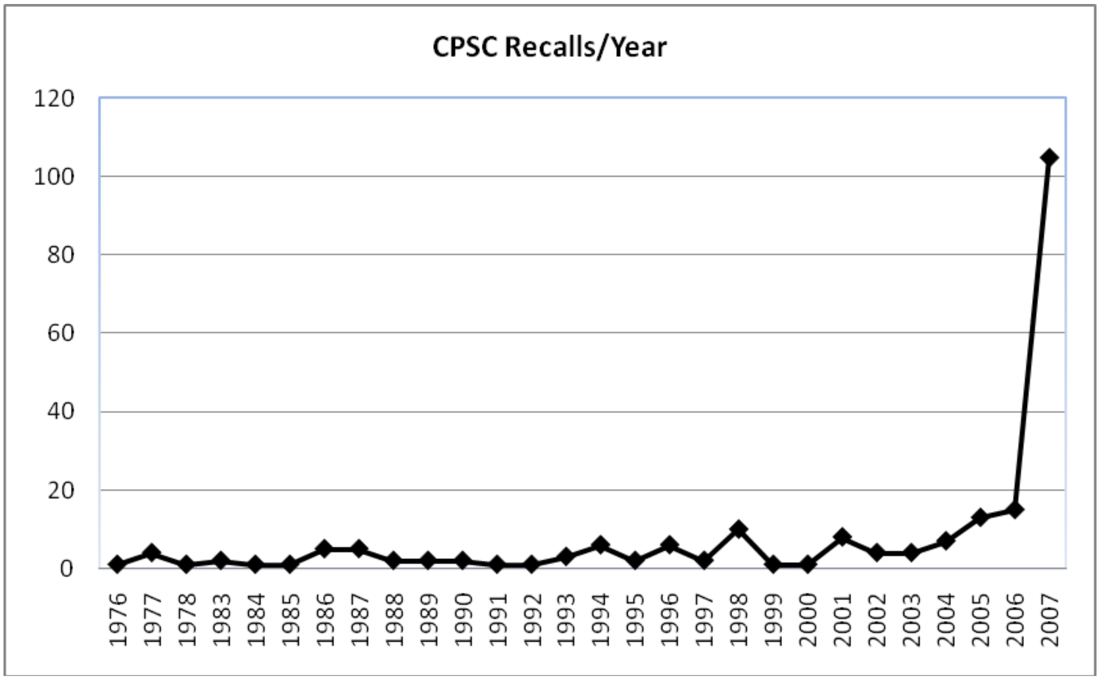
[29] www.cpsc.gov/businfo/cpsa.html (Accessed 09/17/08)

Figure 2.0 illustrates the total number of CPSC recalls per year of toys and infants/children's products. The author attributes the large spike in 2007 to increased scrutiny of imported and domestic consumer goods due to increased non-governmental organizations (NGO) and governmental agency(s) diligence.

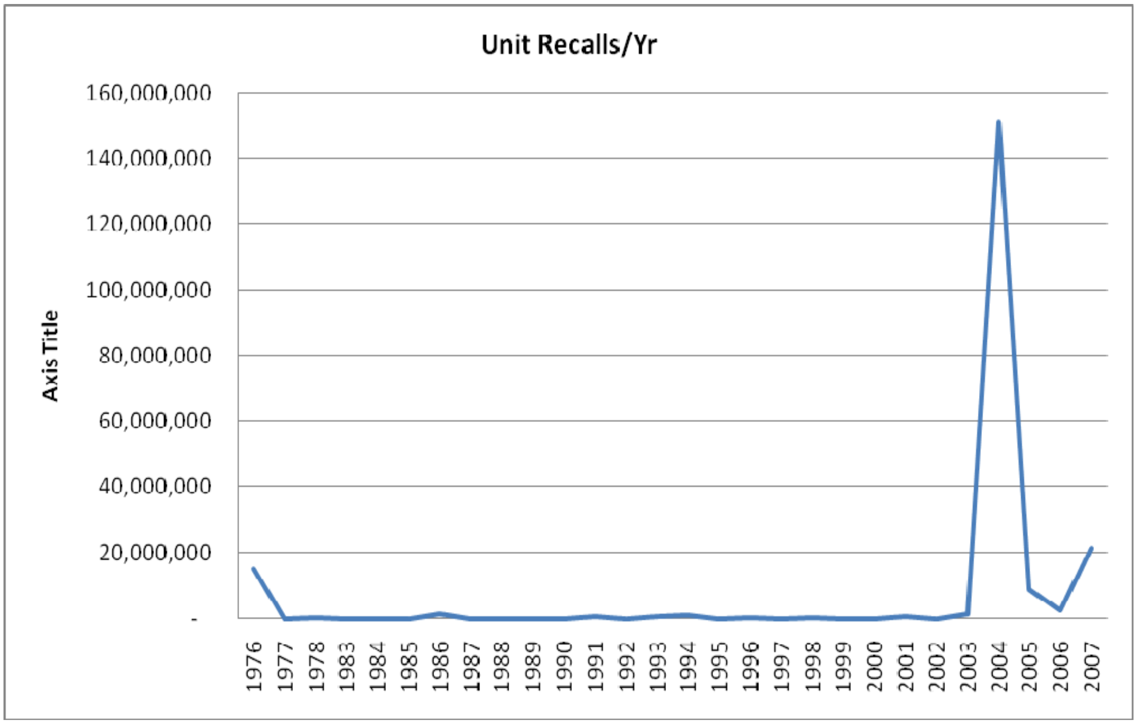
Figure 2.0



Data obtained from CPSC website and compiled/plotted by author

Figure 3.0 represents the total number of CPSC unit recalls per year of toys and infants/children's products. The 2004 peak represents a 150,000,000 unit recall of children's metal toy jewelry intended for vending machine point-of-sale. Due to the magnitude of units recalled and supplier's geographic locations, CPSC did not provide country of manufacture data.

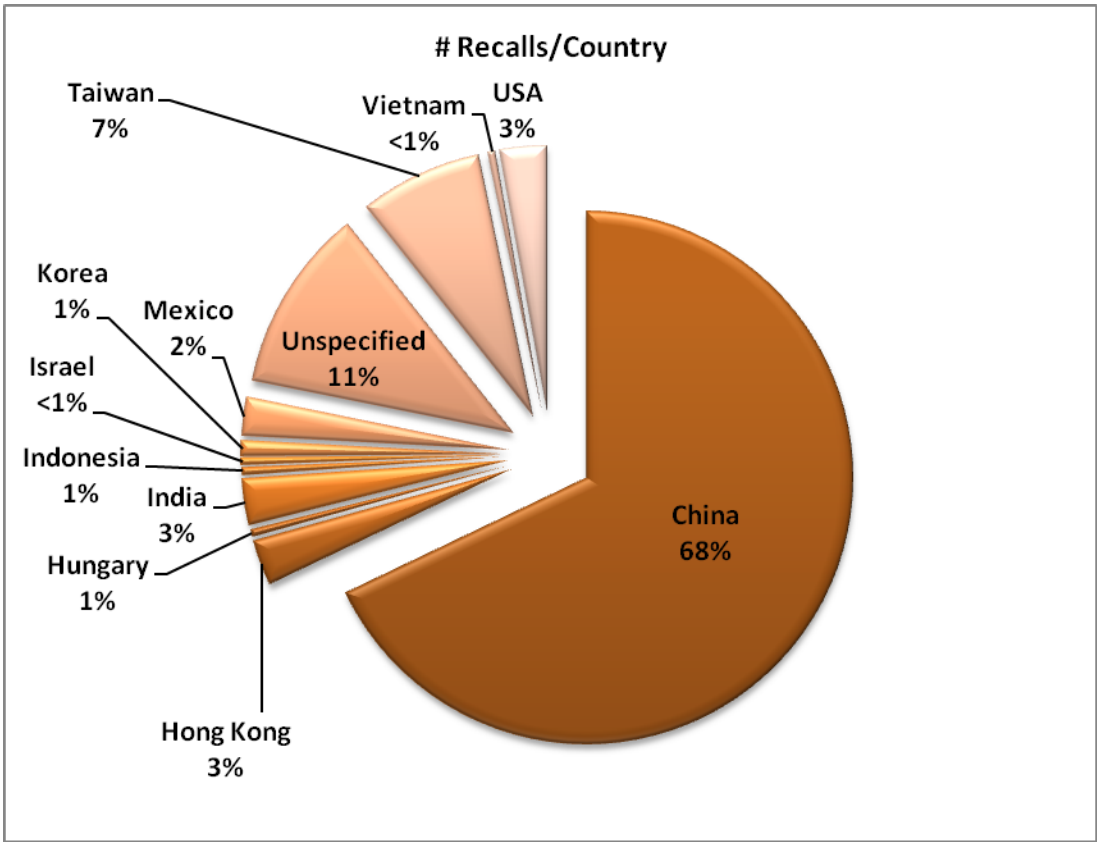
Figure 3.0



Data obtained from CPSC website and compiled/plotted by author

The Figure 4.0 pie-chart delineates a country-specific representation of CPSC recalls per year of toys and infants/children's products. China has clearly staked claim as the unenviable leader in this category and the author attributes this ranking due to sheer volume of in-scope products manufactured in the country.

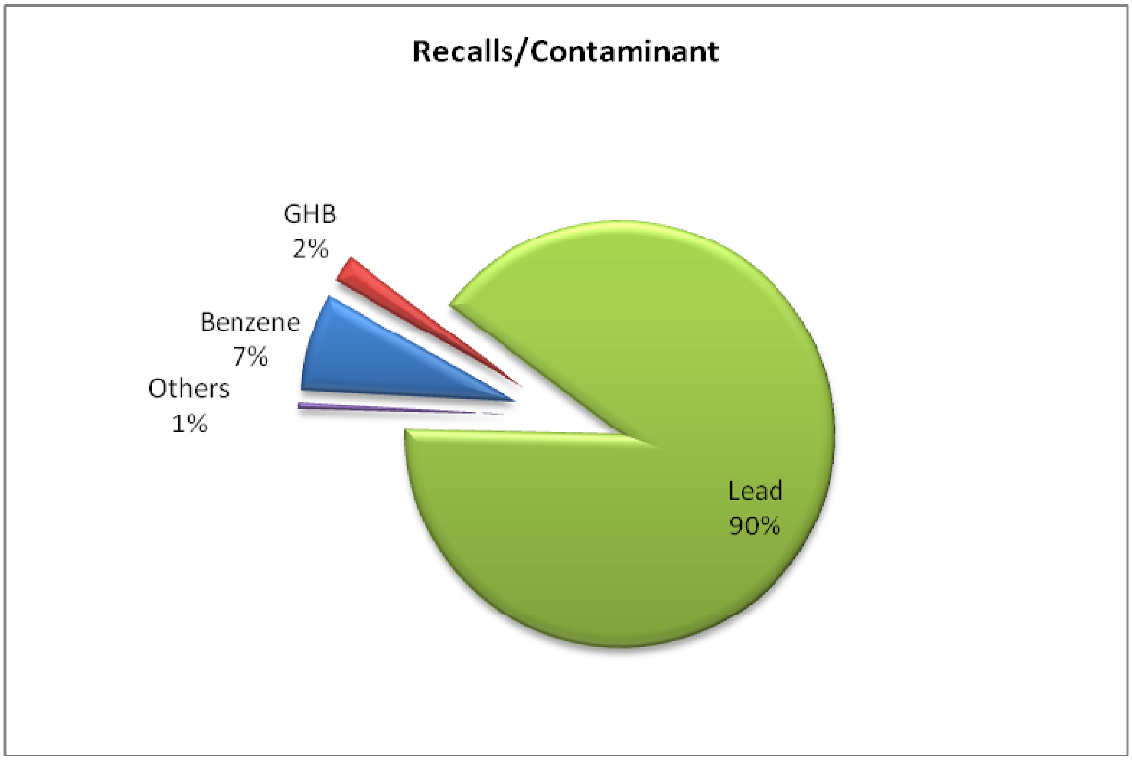
Figure 4.0



Data obtained from CPSC website and compiled/plotted by author

Figure 5.0 exemplifies the overall contributing percentage of CPSC toys and infant/children's product recalls by hazardous contaminant. The fact that only two of the eight RCRA heavy metals, arsenic (As) and lead (Pb), were attributed to CPSC recalls was surprising as the other six may be found as cross-contaminants or functional components in certain alloys, solders, pigments, plated finishes and inks.

Figure 5.0



Data obtained from CPSC website and compiled/plotted by author

Key information obtained from this toy and infant/children's products recall analysis indicates that Asia poses the greatest risk for producing contaminated product as banned by the CPSC and that lead (Pb) is the primary contaminant of concern. This does not preclude non-Asiatic products from further analysis or limit the analytes-of-interest to solely lead (Pb); it does however provide an excellent basis for sample set selection.

2.2 Resource Conservation and Recovery Act – (RCRA)

Congress enacted RCRA on October 21, 1976 as an amendment to the Solid Waste Disposal Act of 1965, in effort to address escalating problems due to increasing volumes of municipal and industrial waste. It mandated that hazardous wastes be treated, stored and disposed of so as to minimize the present and future threat to human health and the environment and imposed strict management standards on hazardous waste generators and transporters, as well as owners of treatment, disposal and storage facilities (TSDFs).[30] The first RCRA regulations were published in the federal register on May 19, 1980 and established the "cradle-to-grave"[31] management system still utilized today. Since initial promulgation, RCRA has been amended three-times: the Hazardous and Solid Waste Amendments of 1984; the Federal Facility Compliance Act of 1992; and the Land Disposal Program Flexibility Act of 1996.

Though RCRA encompasses a plethora of management standards regarding all aspects of hazardous waste, a key focal point of this research was to examine the attributes that relegates a waste to hazardous status. Since the regulatory definitions of "solid waste" and "hazardous waste" are narrower in scope than the statutory definitions and the regulations are what governed parties manage to, the statutory designations have been excluded. For an entity to be considered as a potential hazardous waste, it must first meet the RCRA §261.2(a)(1) definition of a "solid waste" paraphrased below:

> …*any garbage, refuse, sludge from a waste treatment plant, water supply treatment plant or air pollution control facility and other discarded material, including solid, liquid, semisolid, or contained gaseous*

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[30] Thomas F.P. Sillivan *Environmental Law Handbook – 19th Ed (*Rowman & Littlefield, 2007), 133.

[31] "Cradle-to-grave" is considered from the point of waste generation to its ultimate disposal; however the original generator of hazardous waste does not relinquish liability upon disposal.

> *materials, resulting from industrial, commercial, mining and agriculture activities and from community activities but does not include solid or dissolved material in domestic sewage, or solid or dissolved materials in irrigation return flows or industrial discharges which are point source subject to permits under section 402 of the Federal Water Pollution Control Act, as amended, or source, special nuclear, or byproduct material as defined by the Atomic Energy Act of 1954, as amended.*[32]

Provided the entity satisfies "solid waste" criteria and it is not excluded from regulation per §261.4(b), it must be evaluated against RCRA Subtitle C *listed* or *characteristic* hazardous waste criteria. Listed wastes are those which EPA has specifically determined are hazardous and have assigned F, K, P or U waste codes to delineate. Table 2.0 illustrates the RCRA *listed* waste codes.

Table 1.0
Listed RCRA Hazardous Waste Codes

Waste List	Type	Description	Citation
F	Non-specific sources	Wastes from common manufacturing & industrial processes which can occur in different industry sectors	40 CFR §261.31
K	Source-specific wastes	Wastes from specific industries, including but not limited to, petroleum refining, pesticide manufacturing, pigments.	40 CFR §261.32
P	Discarded commercial chemical products	Acutely hazardous waste of commercial chemical products, off-specification or expired products, container residues or spill residues	40 CFR § 261.33
U	Discarded commercial chemical products	Toxic hazardous waste of commercial chemical products, off-specification or expired products, container residues or spill residues	40 CFR § 261.33

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[32] Thomas F.P. Sillivan *Environmental Law Handbook – 19th Ed (*Rowman & Littlefield, 2007), 137.

In event that a solid waste is not a listed hazardous waste, it must also be evaluated against the following four (4) EPA-specified *characteristics* to determine if hazardous via corrosivity, ignitability, reactivity and toxicity. Table 3.0 details the RCRA characteristic hazardous waste criteria.

Table 2.0
Characteristic RCRA Hazardous Waste Codes

Characteristic	Hazard Code	Criteria	Citation
Ignitable	I	• Liquid containing <24% alcohol by volume with f.p. <140°F • Non-liquid capable under STP, of causing fire through friction, absorption of moisture or spontaneous chemical changes, and when ignited, burns so vigorously and persistently that it creates a hazard • Ignitable compressed gas as defined by USDOT in sufficient quantity to present danger to human health and the environment (49 CFR §173.115) • Oxidizer defined by USDOT Hazardous Materials Regulations (49 CFR §173.127)	40 CFR §261.21
Corrosive	C	Aqueous liquid of pH ≤2 and ≥12.5 or corrodes SAE 1020 steel >0.25 inch/year @ 130°F	40 CFR §261.22
Reactive	R	• Unstable and readily undergoes violent change without detonation • Reacts violently with water • Forms potentially explosive mixtures with water • If mixed with water, generates toxic gases, vapors, or fumes in sufficient quantity to present danger to human health and the environment • Cyanide or sulfide bearing waste, which when exposed to pH conditions between 2 - 12.5, can generate toxic gases, vapors or fumes in sufficient quantity to present danger to human health and the environment • Capable of detonation or explosion if subjected to strong initiating source or if heated in confinement • Capable of detonation or explosive decomposition or reaction at STP • Forbidden Class A or B explosive as defined per USDOT Hazardous Materials Regulations (49 CFR 173.50 – 173.58)	40 CFR § 261.33
Toxic	E	Solid waste, of which the extract obtained from EPA Method 1311 toxicity characteristic leaching procedure (TCLP) equals or exceeds the specified regulatory level	40 CFR § 261.24

In view of the fact that this research focused solely on RCRA metals in infants/children's products and toys and there are no *listed* waste codes defined for these entities, nor are the metals ignitable, reactive or corrosive, then through default the *toxicity* characteristic is the foci. *SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* is the United States Environmental Protection Agency's (USEPAs) official compendium of analytical and sampling methodologies that have been evaluated and approved for use in complying with the RCRA regulations; within which is contained EPA Method 1311 *Toxicity Characteristic Leaching Procedure (TCLP).* The TCLP analysis is a simulated landfill procedure designed to determine the mobility of organic and inorganic contaminants in liquid, solid or multiphasic waste forms.[33] RCRA metals analysis utilizes a mildly acidic acetic acid extraction fluid at a 20:1 liquid/solid ratio for a 16 – 18 hour extraction period. Metallic analytical determinations require the extract to be acidified with nitric acid to a pH <2.0 prior to aliquot analysis via EPA method 6010B or 7000 series for speciated leachable metals concentrations.

Due to stringent sample preparation requirements, the cost of a TCLP analysis is considerably higher than that of a non-liquid total metals analysis per Method 3050, thus the latter if often chosen as a TCLP screening method cost-savings measure. Provided the total metals analyte yield is less than twenty-times (20x) the TCLP regulatory level, a TCLP extraction is unnecessary as the value cannot be exceeded due to the 20:1 dilution factor; yields greater than 20x do however require Method 1311 extraction for substantiation. Table 3.0 illustrates the maximum concentration of RCRA-metals contaminants and applicable hazardous waste (HW) codes for the toxicity characteristic.

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[33] http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/1311.pdf (Accessed 9/20/08)

In effort to determine correlation between FPXRF, total metals and TCLP yields, all three analytical methodologies have been performed in this research and the results reported in Tables 5.0 & 6.0.

Table 3.0
RCRA Metals Waste Codes and Action Levels

Contaminant	CAS #	EPA Hazardous Waste Code	Regulatory Level (mg/L)
Arsenic	7440-38-2	D004	5.0
Barium	7440-39-3	D005	100.0
Cadmium	7440-43-9	D006	1.0
Chromium	7440-47-3	D007	5.0
Lead	7439-92-1	D008	5.0
Mercury	7439-97-6	D009	0.2
Selenium	7782-49-2	D010	1.0
Silver	7440-22-4	D011	5.0

2.3 Field Portable X-Ray Fluorescence

2.3.1 History

Since Noble-prize winning physicist Wilheim Roentgen's 1895 discovery of 'a new kind of rays', [subsequently dubbed X-rays], the field of X-ray fluorescence spectrometry has continuously evolved as the desire to bring the analytical instrument to the sample grows stronger. Upon Roentgen's first X-ray photograph of his wife's hand, the significance of this discovery was immediately realized as university laboratories delved into comprehensive research efforts.[34]

In 1913, two significant, yet independent discoveries by Henry Gwynn Jeffreys Moseley and W.D. Coolidge helped further advance the field of X-ray fluorescence spectrometry. Moseley recognized a relationship between wavelength of X-ray spectral lines and elemental atomic number, thus providing the groundwork for both qualitative

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[34] Stanislaw Piorek.. "Field Portable X-ray Fluorescence Spectrometry: Past, Present, and Future", *Field Analytical Chemistry and Technology*, Vol.1, 6, 317-329, (1997). http://ill.rit.edu. (Accessed 10/07/08)

and quantitative X-ray analysis. His work concluded that X-ray spectrum K-line transitions moved consistently with atomic number (Z) increases of one. The relationship is expressed in Figure 6.0.[35] It was this discovery which led to the periodic table being arranged by atomic number versus atomic weight.[36]

Figure 6.0

$$c/\lambda = a\,(Z-\sigma)^2$$

a = proportionality constant

σ = periodic series constant

Coolidge's invention of the first hot-filament, high-vacuum X-ray tube was monumental as the equipment allowed for solids or powders to be placed on the anode target while recording corresponding characteristic spectra on photographic film.[37]

Through subsequent years, numerous significant advancements set the stage for our current position: (1928) Geiger and Muller's gas-filled detector yielding steadily reproducible results; (1948) Friedman and Brinks build first commercial X-ray spectrophotometer prototype; (1948) transistor is invented, spawning field of semi-conductors; (1953) radioisotope sources utilized as means of sample excitation and allowed for first battery-powered portable devices; (1960s) the first generation wavelength dispersive FPXRF is introduced; (1975) the personal computer is born; and (1978, 1984 and 1995) the second, third and fourth generation FPXRFs are conceived

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[35] http://karlloren.com/ultrasound/p50.htm (accessed 10/02/08)
[36] http://learnxrf.com/History.htm (accessed 10/02/08)
[37] Piorek, S., 317

respectively. In Figure 7.0 below, Piorek does an excellent job illustrating the history of significant technological milestones leading to development of FPXRF we know today.[38]

Figure 7.0

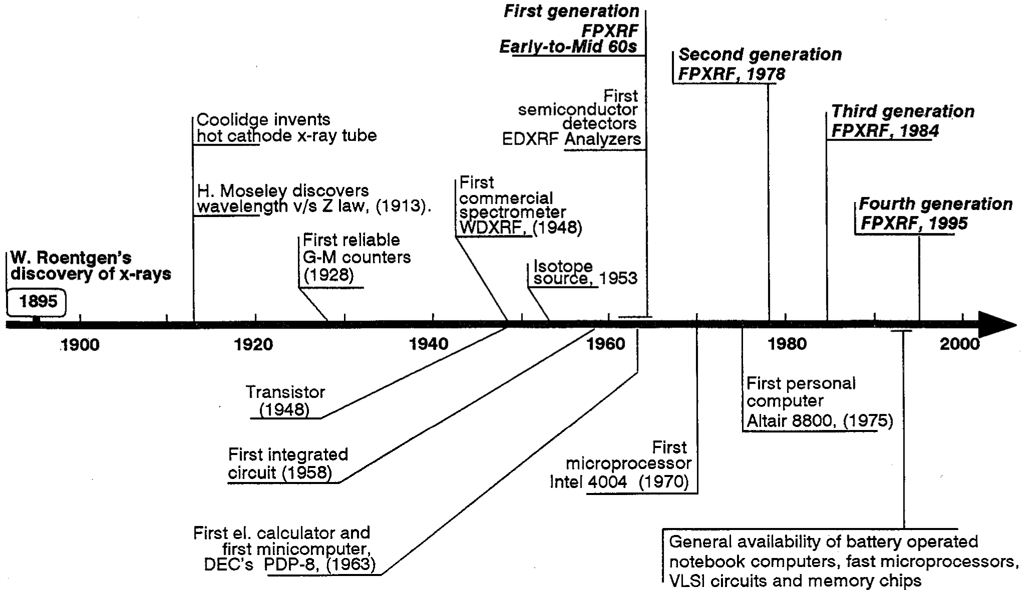

FIG. 7. FPXRF timeline—milestones leading to the development of FPXRF analyzer.

Noteworthy is the fact that the preceding historical data, though representative of FPXRF, does not necessarily reflect the chronology of the focal point of this research - <u>tube-based</u> FPXRF devices. The author, through extensive research and interviews with market-leading equipment manufacturers, was unable to ascertain objective, published evidence pinpointing the date of first commercial availability or manufacturer for a tube-based FPXRF unit. Anecdotal data however indicates circa 2001.

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[38] Piorek, S., 320

2.3.2 Principle of Operation

Tube-based FPXRF functions via the known principle that an electron will be ejected from one of its atomic orbitals (K, L, M…), if excited by an incident photon of greater energy than the electron binding energy to the atomic nucleus. Upon inner K-orbital electron ejection, de-excitation occurs in which a higher energy outer L-orbital electron is transferred to the vacant position as the ejected electron leaves the atom as a fluoresced light wave, called the characteristic X-ray of the element. The same principle applies for the outer shell orbitals as the M-orbital electron will replace the L-orbital electron than has filled the vacancy of the K-shell, thus yielding the K and L characteristic x-rays for FPXRF analysis. Since the energy of the ejected photon equals the differential energy between the K and L orbitals and those energies are always the same for a specific element, (the element's 'characteristic'), one may identify an element by measuring the wavelength of fluoresced X-ray light (photon).[39]

It is important to note that a tube-based FPXRF device possesses both qualitative and quantitative capabilities. The X-ray spectrum obtained during the measurement process yields multiple characteristic peaks, all of differing energies and each representing a distinct element. Therefore, by detecting and processing these characteristic photon peaks, a qualitative elemental composition of the sample is produced. Quantitatively, individual element concentration is determined by measuring the number of ejected photons over a period of time, in which analyte presence is proportional to peak intensity.[40]

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[39] http://www.learnxrf.com/History.htm (accessed 10/02/08)

[40] http://omega.physics.uoi.gr/xrf/english/the_xrf_technique.htm (accessed 09/23/08)

Prior to commercially-available tube-based FPXRF introduction around 2001, traditional field-portable XRF equipment relied on radioisotopes such as cadmium $(Cd)^{109}$, americium $(Am)^{241}$, cobalt $(Co)^{57}$, iron $(Fe)^{55}$ or combinations thereof as the primary excitation source. Though rugged and reliable, the potential for radiation exposure through improper handling, device leakage and haphazard disposal practices, in addition to robust regulations and strict licensing protocols, limited use to only credentialed and licensed professionals. Incorporation of miniaturized X-ray tubes into FPXRF instruments not only alleviated the difficulties and stigma associated with isotope devices, but also shortened sampling cycles and increased sensitivity as the output can be adjusted to specific target analytes.[41]

The tube-based FPXRF devices of today are known as fifth generation equipment, consisting of three primary components – the excitation source, detector and microprocessor.[42] As the name implies, tube-based devices utilize a battery-powered, miniature X-ray tube as the incident X-ray source to bombard and dislodge inner orbital electrons. The fluoresced X-rays (photons) are then simultaneously captured by the detector, are amplified and the characteristic peaks analyzed by the unit's microprocessors to yield elemental characterization and concentration. Figure 8.0[43] illustrates the affects of incident X-rays on an atom, while Figure 9.0[44] provides a representative overview of the entire tube-based FPXRF analytical process.

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[41] http://www.eponline.com/articles/53690/ (accessed 10/02/08)

[42] Pete Palmer, Siri Webber and Kelly Ferguson. "ON THE SUITABILITY OF PORTABLE X-RAY FLUORESCENCE ANALYZERS FOR RAPID SCREENING OF TOXIC ELEMENTS", *Laboratory Information Bulletin # 4376,* pp. 1-15. http://bss.sfsu.edu/envstudies/files/faculty_research/palmer_lib-xrf_suitability.pdf (accessed 10/02/08)

[43] http://www.niton.com/Portable-XRF-Technology/how-xrf-works.aspx (accessed 09/23/08)

[44] http://omega.physics.uoi.gr/xrf/english/the_xrf_technique.htm (accessed 09/23/08)

Figure 8.0

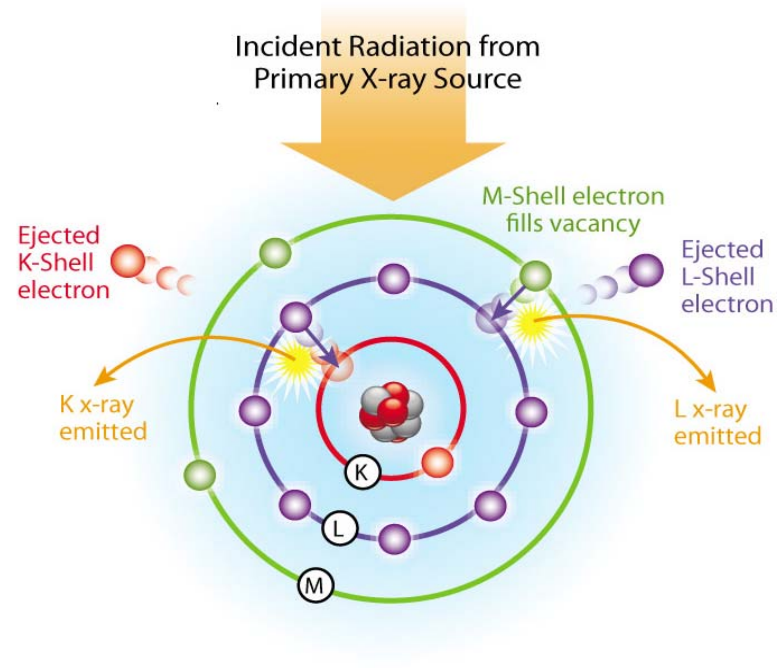
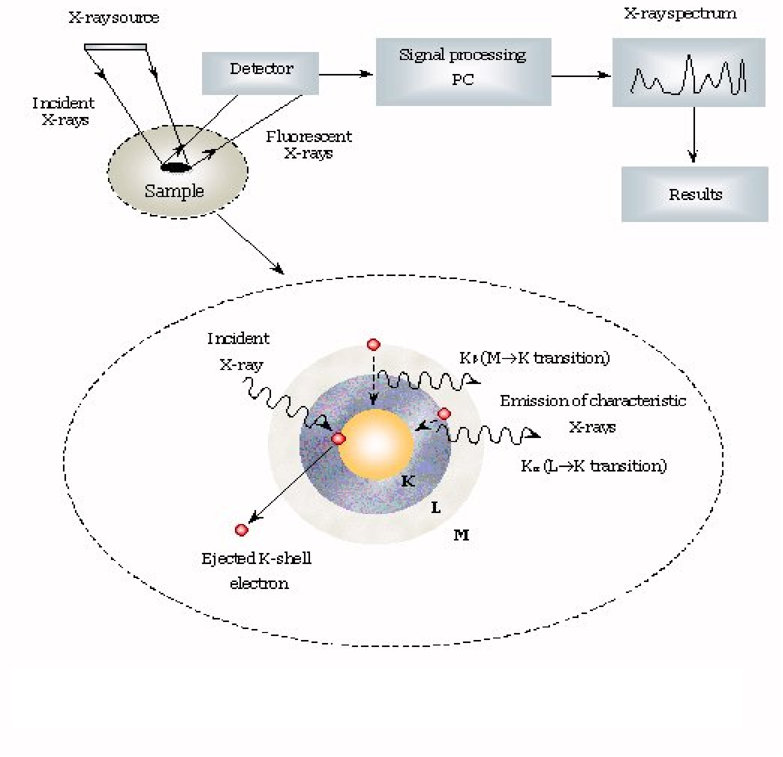

Incident Radiation from
Primary X-ray Source
M-Shell electron
fills vacancy
Ejected
K-Shell
electron
Ejected
L-Shell
electron
K x-ray
emitted
L x-ray
emitted
K
L
M

Figure 9.0



Since introduction less than a decade ago, the cost of tube-based FPXRF has consistently decreased while device capabilities have experienced the inverse. Typical commercial price ranges are approximately $25,000 - $60,000 and vary in accordance with brand name and sophistication.[45] Additionally, manufacturers continue to improve on existing technologies and are developing new ones as well, such as light elements analysis; the objective being to create a truly "point-and-shoot" portable analytical device.

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[45] Author's personal experience with tube-based FPXRF procurement at his place of employment

Literature Review

3.1 FPXRF Applications

Though utilization and acceptance of XRF analysis is not new to the scientific community, the use and endorsement of field portable (a.k.a. - portable or handheld) x-ray fluorescence (FPXRF) equipment is a comparatively novel concept. However, it appears environmental professionals, geologists, industrial hygienists, chemical engineers, materials specialists and numerous other scientific disciplines and consumer advocacy groups are warming up to this technology and embracing it as a viable, qualitative screening tool for employment in their respective areas. The subsequent sections delineate today's more common applications of FPXRF, but by no means are exclusive of the infinite potentials.

3.1.1 Alloy Identification

FPXRF instruments are employed on a daily basis in Russia for inspection of hundreds of in-situ metal samples for alloy verification by customs.[46] The chemical processing and refining industries utilize portable XRF for in-situ alloy identification during routine operation and maintenance (O&M) activities. Since these facilities literally contain miles of piping and tubing and require almost continuous operation, it is unrealistic to shut-down operations to remove a sample for laboratory analysis; thus field-verification of the material grade is necessary to assure correct replacement

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[46] A.K Khusainov and others, "Portable and X-ray analyzers based on CdTe p-i-n detectors", *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment,* 428, no. 1 (1999). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 01/03/08).

specification.[47] The author, during current employment, has also utilized FPXRF for alloy identification in the electrical connector manufacturing sector where bar and coil stock raw alloys of aluminum, magnesium, steel, titanium, copper, brass, zinc and stainless steel are ubiquitous throughout the manufacturing floor. Material misplacement or failure to properly label "tail-pieces"[48] could result in unauthorized alloy utilization in hi-reliability components, thus confirmatory analysis via handheld XRF is carried out.

The EU RoHS Directive has also played an integral role in the promotion of FPXRF technology for alloys identification in electrical and electronic equipment due to the limitations set forth and also specific materials exemptions contained in the regulation's annex. Though amendment 2005/617/EC proclaims a "homogenous material"[49] shall not contain >0.1% by weight (w/w) Cr^{+6}, Pb, Hg, PBB or PBDE or >0.01% w/w Cd, certain material exemptions are authorized. Steel, aluminum and copper alloys may contain [Pb] up to 0.35%, 0.4% and 4.0% w/w respectively,[50] whereas electrical and electronic equipment (EEE) containing solely high-leaded solders exceeding >85% [Pb] are also considered 'compliant by exemption'.[51]

In evaluating the viability of handheld XRF as a practical screening tool for detection of hazardous substances in electronic equipment, Shrivastava et al., concluded that FPXRF is a suitable screening tool for [Pb] and [Cd] with some limitations. Test samples were obtained from various electronic products and underwent little or no

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[47] Tim McGrady, Director of Product Compliance, N.A., LG USA, Interview by author, February 5, 2008. Tape recording.

[48] Residual material portion leftover from a batch processing lot that may not carry the same identification markings as the initial work piece

[49] Cannot be "mechanically disjointed or separated"

[50] EU Directive 2002/95/EC Annex http://eur-lex.europa.eu/pri/en/oj/dat/2003/l_037/l_03720030213en00190023.pdf (Accessed 5/5/08)

[51] EU Directive 2002/95/EC Annex http://eur-lex.europa.eu/pri/en/oj/dat/2003/l_037/l_03720030213en00190023.pdf (Accessed 5/5/08)

sample preparation during XRF testing - the purpose of this methodology was to mimic FPXRF in-situ screening conditions. Following XRF analysis of thirty-five (35) samples, three-times for 180 seconds each, identical samples were then sent to independent testing labs for confirmatory analysis via ICP-AES in accordance with EPA Method 3050B. For most samples, cadmium and lead FPXRF data correlated with the lab ICP-AES yields, however some exceptions were present. With FPXRF, determining concentrations above the RoHS limits of 1000 ppm [Pb] and 100 ppm [Cd] in a homogenous material was forthright, but difficulties were encountered for lower cadmium concentrations. Lead [Pb] detection was consistent with independent laboratory ICP-AES yields, but FPXRF had the tendency to consistently overestimate lead.[52]

Though the work illustrates correlation between FPXRF and ICP-AES, the author disagrees with the comparative methodologies utilized. XRF analysis of a solder joint will, depending on volume, yield elemental constituents of the alloy only, whereas Method 3050B requires homogenization via grinding prior to acid-digestion and analysis. Unlike XRF which is non-destructive, Method 3050B requires a representative sample for destructive analysis and it is at this point – sample collection – where the divergence occurs. Obtaining a solder-joint sample from a printed wire board (PWB) often involves a core sample around the joint interface to be taken and for the entire thickness of the board. Thus, the original intermetallic solder joint is now doped with PWB constituents such as pre-preg, copper laminate, resin, soldermask, nomenclature ink; all of which serve as diluents to the solder alloy component during homogenization and digestion.

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[52] Puneet Shrivastava, Scott O'Connell and Allen Whitley PhD. "Handheld X-ray Fluorescence: Practical Application as a Screening Tool to Detect the Presence of Environmentally-Sensitive Substances in Electronic Equipment", *ISEE 2005, pp 157-162*

3.1.2 Consumer Goods

Ironically, although the multitude CPSC recalls related to lead [Pb] in consumer goods - specifically those targeted towards children - have prompted removal of millions of discrepant products from interstate commerce, little validated, peer-reviewed and published literature regarding FPXRF and consumer product analysis was available. Non-governmental organizations (NGOs) and consumer advocacy groups such as Greenpeace,[53] Toxin Free Toys,[54] Safe Toys,[55] Healthy Toys,[56] and W.A.T.C.H. (World Against Toys Causing Harm)[57] all allude to portable XRF product testing on their websites, however raw substantiating data and methodologies are absent. Weidenhamer, Clement and Yost of Ashland University have conducted extensive research resulting in four published works[58,59,60,61] on the subject matter of determining the contamination source (electronic solder a/o lead battery waste) of low-cost jewelry; however all analyses were performed via flame atomic adsorption spectroscopy (FAAS) without preliminary FPXRF screening.[62]

In research published by Netherlands FPXRF equipment manufacturer PANalytical, certified reference materials (CRM) were utilized to calibrate an Epsilon 5 spectrometer in effort to evaluate the instrument's capabilities for characterizing

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[53] www.greenpeace.org (Accessed 04/16/08)

[54] www.toxinfreetoys.com (Accessed 04/16/08)

[55] www.safetoys.com (Accessed 04/16/08)

[56] www.healthytoys.org (Accessed 04/16/08)

[57] www.toysafety.org (Accessed 04/16/08)

[58] Jefferey D. Weidenhamer and Michael L. Clement. "Widespread lead contamination of imported low-cost jewelry in the U.S.", *Chemosphere*, 67, (2007). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 04/16/08)

[59] Jefferey D. Weidenhamer and Michael L. Clement. "Leaded electronic waste is a possible source material for lead-contaminated jewelry", *Chemosphere*, 69, (2007). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 04/16/08).

[60] Jefferey D. Weidenhamer and Michael L. Clement. "Evidence of recycling of lead battery waste into highly leaded jewelry", *Chemosphere*, 69, (2007). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 04/16/08)

[61]. Jamie L Yost and Jefferey D. Weidenhamer. "Lead contamination of inexpensive plastic jewelry", *Science of the Total Environment*, 393, (2008). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 04/16/08)

[62] Ibid – footnotes 39-41

polyethylene materials. The CRMs - a total of five - contain the target elements Cr, Hg, Cd, Pb, As, Ni, Cu, Zn, Br and Ba.[63] Samples were analyzed a total of twenty-times for 600 seconds each to determine accuracy and precision, both of which were determined to meet specified parameters.[64] Although the application does not directly address consumer goods, it does indirectly validate that FPXRF is a viable screening tool for consumer goods comprised of homogenous polyethylene materials.

The only literature directly aligned to FPXRF screening of consumer goods, specifically electronics, was alluded to briefly in section 3.1.1., concerning alloy identification. Shrivastava, O'Connell and Whitely examined [Pb] and [Cd] in thirty-five (35) electronic components, ranging from peripheral cords to microphones to cables to circuit boards (PWB).[65] Maintaining continuity with this subsection, only cables, cords and the microphone will be discussed as they are individually purchasable entities located external to the electronic products from which they were obtained. In other words, they are not contained within an assembly and possess a higher degree of human contact potential than a PWB or resistor. Portable-XRF sample preparation consisted of removal of outer jacketing from copper wire on cables and cords to generic methodologies such as ensuring the sample blocks the probe opening entirely.[66] Interestingly, although FPXRF sample preparation specified removal of cable jacketing, the off-site ICP-AES analysis parameters states that "different cables were tested as they have historically contained

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[63] Joanna Wolska. "Safeguarding the environment – XRF analysis of heavy metals in polyethylene*," Plastics Additives & Compounding*, January/February 2005, pp.36-39.

[64] Ibid

[65] Puneet Shrivastave, Scott O'Connell, and Allen Whitley Ph.D.. "Handheld X-ray Fluorescence: Practical Application as a Screening Tool to Detect the Presence of Environmentally-Sensitive Substances in Electronic Equipment", *ISEE 2005* pp. 157-162.

[66] Ibid

heavy metals as PVC stabilizers."[67] In addition to my disagreement between FPXRF and ICP-AES analysis homogenization requirements specified in section 3.1.1., the aforementioned statement appears incongruous between specified sample preparation protocols for cables and actual occurrence. It is unclear from the Table IV whether portable XRF analysis represents that of homogenous copper wire only and if ICP-AES represents bare wire or homogenized jacketed wire. Thus, due to these inconsistencies the viability of FPXRF yields in comparison to confirmatory ICP-AES analysis is indeterminable.

3.1.3 Cultural Studies

Widespread utilization and growing popularity of portable XRF equipment in the archaeological and cultural studies arenas was an unanticipated research find. However, upon obtaining a deeper understanding of the non-destructive, in-situ, multi-elemental analytical requirements necessary in these fields, the application's vagueness was clarified. Field portable XRF has been effectively used to characterize metallic-based ceramic pigments, to characterize compositions of ancient ceramics, and to differentiate original artworks from forgeries or reproduction pieces.[68,69,70] It is considered a non-destructive analytical technique because during standard measuring conditions, the energy transferred to the target sample is minimal.[71]

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[67] Ibid

[68] J. Pérez-Aranegui, J., et al., "Characterization of pigments found in traditional Valencian ceramics by means of laser ablation-inductively coupled plasma mass spectrometry and portable X-ray fluorescence spectrometry", *Talanta, 74,* 2008, http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 04/18/08)

[69] D.N. Papadopoulou, "Comparison of portable micro-X-ray fluorescence spectrometry with inductively coupled plasma atomic emission spectrometry for the ancient ceramics analysis", *Spectrochemia Acta Part B,59 (2004).* http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 04/18/08)

[70] Z. Szökefalvi-Nagy, Z. et al., "Non-destructive XRF analysis of paintings", *Nuclear Instruments and Methods in Physics Research Section B,226,(* 2004). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 04/18/08)

[71] Ibid

Hungarian researchers utilized a 3 mm spot-diameter XRF to determine the authenticity of work by two artists - Géza Mészöly (1844-1887) and Tivadar Csontváry-Kosztka (1853-1919) - through identification for the presence of titanium [Ti] at white colored spots.[72] Artworks absent of telltale signs such as poor quality, cracking, or paint stratification differences usually cannot be authenticated via an expert naked eye, therefore compositional analysis is required. In their work, Szökefalvi-Nagy, et al., based authentication parameters on the fact that titanium dioxide [TiO_2] only became available around 1920, thus detection of its presence for works completed prior is indicative of forgery or repainting. Their XRF analysis illustrates that the presence of [Ti] does not automatically disqualify a pre-1920 work though, as white barium-based paints were also frequently used and considerable difficulty exists differentiating between overlapping Ti K-orbital x-rays and those emitted from Ba L-orbitals.[73] In the Mészöly case, a certified original was used as reference and contained no [Ti], thus the others were ruled as forgeries.

In Spain, Pérez-Agantegui, et al., performed a comparative study utilizing both portable XRF and laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS) to chronologically characterize cobalt [Co] pigments contained in Valencian ceramics. Ten ceramic fragments containing cobalt pigment decoration were analyzed by portable XRF with a 3 mm collimated beam and total acquisition time of 300 seconds.[74] Background levels were established by obtaining three samples each from the pigmented areas and non-pigmented areas in order to differentiate both glaze and pigment

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[72] Ibid

[73] Ibid

[74] J. Pérez-Arantegui, et al., "Characterization of pigments found in traditional Valencian ceramics by means of laser ablation-inductively coupled plasma mass spectrometry and portable X-ray fluorescence spectrometry", *Talanta,* 74, 2008. http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 04/18/08)

compositions. LA-ICPMS followed thereafter as the ablation process is considered slightly destructive. The presence of cobalt, as well as copper and manganese, was determined in all analyzed pigment samples and good agreement between portable XRF and LA-ICPMS was illustrated in addition to conclusions drawn. However, reliability of portable XRF results for samples with low-cobalt concentrations (approaching the equipments limit of detection) was lower than LA-ICPMS.[75] This concept is reinforced through the work Shrivastava, et al., which also concluded that XRF reliability decreases proportionally to target analyte concentration. Both techniques were deemed viable means of characterizing ceramic pigments, however there were associated advantages and disadvantages of each. Though portable XRF is non-destructive, cost-effective, in-situ and capable of providing results at the mg g^{-1} level, the destructive, non-portable and expensive LA-ICPMS provides better detection limits and spatial resolution.[76]

Continuing the research of comparative analytical techniques for characterization of ceramics, Papadopoulou, D.N., et al., investigated the capabilities of portable XRF in concurrence with ICP-AES for multielemetal, in-situ quantification of silicon [Si], iron [Fe], calcium [Ca], potassium [K], manganese [Mn] and titanium [Ti].[77] Sample preparation for XRF analysis consisted of mechanical removal of the external layer and also homogenized pelletization of sub-samples <93 μm average grain size. ICP-AES sample preparation consisted of sub-sample grinding and microwave digestion via a mixture of nitric and hydrofluoric acid – the latter to liberate silicate bound metals.[78] Six 'surface-prepared' ceramic sample pieces and their corresponding sub-sample pellets

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[75] Ibid

[76] Ibid

[77] D.N Papadopoulou.. "Comparison of portable micro-X-ray fluorescence spectrometry with inductively coupled plasma atomic emission spectrometry for the ancient ceramics analysis", *Spectrochemia Acta Part B,* 59, (2004). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 04/18/08).

[78] Ibid

were analyzed for 300 seconds each via portable XRF with a total of 10 measurements performed on each sample and the mean value reported. Significant statistical differences (95% CI) are present when comparisons between the elemental means obtained by XRF-surface, XRF-pellet and ICP-AES are made.[79] Surface and pellet XRF analysis showed good correlation for fifty-percent of the elements and moderate correlation for another. The research indicates that, although portable XRF yields did not directly correlate with ICP-AES, it is still a beneficial screening tool with respect to its non-destructive and timely analytical capabilities.

3.1.4 Environmental

Utilization of field portable X-ray fluorescence (FPXRF) methodologies affords practicable and efficient in-situ analytical capabilities for a number of differing environmental media.[80,81] In the environmental, health and safety (EH&S) field and at hazardous waste sites across the United States, in-situ FPXRF analysis has been recognized as a proficient, expeditious and inexpensive technique for both screening and quantification of varying types of potentially hazardous materials, including soils, sediments, surface coatings and sludges.

The United States Environmental Protection Agency's Environmental Response Team (USEPA-ERT) reported considerable use of radioisotope-based FPXRF equipment for soil and sediment characterization at hazardous waste and remediation locations

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[79] Ibid

[80] Dennis Kalnicky and Raj Singhvi, "Field portable XRF analysis of environmental samples", *Journal of Hazardous Materials*, 83, no.1-2, (2001). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 01/08/08)

[81] M.B. Bernick, et al., "Results of field-portable X-ray fluorescence analysis of metal contaminants in soil and sediment", *Journal of Hazardous Materials*, 43, (1995). http://library.rit.edu/electronic/scidirect/scidirect.html, (accessed 04/19/08)

throughout the country.[82] In-situ and prepared sample FPXRF analyses were performed and confirmed via off-site chemical analysis in accordance with matrix-specific SW-846 parameters. In-situ sampling required the FPXRF probe be situated flush against the trowel-flattened surface free of organic debris and rocks of considerable size, whereas prepared sample analysis requires drying and sieving prior to placement in an X-ray sample cup. Regression evaluation of in-situ and prepared samples lead [Pb] analysis to atomic absorption (AA) yields indicates similar confirmation slopes and substantiates FPXRF viability as a portable environmental analytical technique.[83]

Published work by UK researchers Killbride, Poole and Hutchings that compares Cu, Pb, Cd, As, Fe, Ni, Mn and Zn analytical yields obtained from both dual-source radioisotope and tube-base FPXRF against Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) indicates linearity for some elements, but not all.[84] Sub-samples from eighty-one (81) soil samples collected at seven industrial sites were air-dried, passed through a 2mm sieve, homogenized via mixing and stored in the dark in sealed plastic bags. Both FPXRF devices, utilizing a 300 second acquisition time, and the lab-based aqua regia methods were evaluated against definitive, quantitative and qualitative relative standard deviation (RSD) limits of ≤10%, <20% and >20% respectively. The dual-source XRF yielded definitive data for Fe, Cu, Pb, Mn, Cd and Zn, whereas only Fe and Pb were met for the tube-based unit.[85] Researchers concluded that analysis time >120 seconds yielded no discernible increases in data quality and that

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[82] Ibid

[83] Ibid

[84] C. Killbride, J.Poole, and T.R. Hutchings, "A comparison of Cu, Pb, As, Cd, Zn, Fe, Ni and Mn determined by acid extraction/ICP-OES and ex-situ field portable X-ray fluorescence analysis", *Environmental Pollution,* .42, no. 1, (2006). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 01/12/08)

[85] Ibid

particle size distribution (<2 μm to >63 μm) did not affect FPXRF yields.[86] The latter is of interest as other works indicate FPXRF vulnerability to physical matrix effects.[87,88] Whether sample preparation efforts definitively mitigated this matrix interference potential remains unknown, but must be considered as a viable possibility.

In one of the most comprehensive publications reviewed to date, Kalnicky and Singhvi examine virtually every aspect of FPXRF applicability towards performing effective contamination delineation, removal and remediation at hazardous waste sites. Ranging from principles of operation to specific FPXRF instruments to calibration, detection limits, sample collection and preparation, QA/QC and overall capabilities, limitations and applications, the work proffers a soup to nuts guide to both radioisotope and X-ray tube-based FPXRF. In covering the aforementioned subject matter, the researchers evaluated the relationship between portable–XRF instrument detection limits (DL) and acquisition time and also examined sample matrix effects to determine if particle size distribution impacts accuracy. Twenty-two (22) discrete elements were analyzed simultaneously using a three-source radioisotope (^{106}Cd, ^{55}Fe and ^{241}Am), portable EDXRF detector in which samples were analyzed 12 times each for durations of 15, 30, 60, 120, 240 and 480 seconds respectively.[89] The vast majority supported the concept that minimum detection limits (MDL) increase proportionally to extended measuring time. Elements which deviated from the above include chromium [Cr] at 30 –

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[86] Ibid

[87] A. Agryaki, M.H. Ramsey and P.J. Potts. "Evaluation of portable X-ray fluorescence instrumentation for in situ measurements of lead on contaminated land," *The Analyst*, 122, (1997). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 04/13/08)

[88] M. Ridings, A.J. Shorter and J.Bawden-Smith. "Strategies for the investigation of contaminated sites using field portable X-ray fluorescence techniques," *Contaminated Site remediation: Challenges Posed by Urban and Industrial Contaminants,* CSIRO, Wembley, Australia, 1999, pp.213-217.

[89] Dennis Kalnicky and Raj Singhvi, "Field portable XRF analysis of environmental samples", *Journal of Hazardous Materials*, 83, no.1-2, (2001). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 01/08/08)

60s, manganese [Mn] at 120 – 240s, arsenic at 30 – 240s, selenium at 30 – 60s and tin [Sn] from 60 - 240s [90].

In the matrix effect evaluation, the same instrument was used to analyze National Institute of Standards and Technology (NIST) soil standard reference materials (SRMs) 2710 and 2711 for the 22 elements of interest.[91] A 60 second 'standard' and 'fine particle' analysis was performed a total of 10 times on each sample type. The 'standard' application was designed to compare laboratory digestion methods for coarse soil, whereas the 'fine' application was reflective of element concentrations in SRMs. The research does not provide sample preparation detail, particle size data or other discernible information to evaluate differences between 'standard' and 'fine particle'. Analytical yields of the fine particle application indicate a higher level of agreement between SRMs than the standard coarse preparation[92], thus indicative that increased sample homogeneity contributes to more accurate FPXRF results.

3.1.5 Geological

Surprisingly, a paucity of published data related to portable XRF and the geological sciences, including mining, was located. Research efforts yielded only two sources which could be declared relevant to this sub-section. The first focuses on a comparative precision study between ICP-AES and XRF, while the second addresses FPXRF and ultrasonic extraction/anodic stripping voltammetry (UE/AVS) field-portable methods at mining sites.

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[90] Ibid
[91] Ibid
[92] Ibid

It must be prefaced that 'XRF' referenced in the work of United Kingdom researchers, Ramsey, et al., does not reflect a field-portable instrument, but instead stationary laboratory equipment.[93] However, since XRF principle of operation is same regardless if the device is fixed or portable, inclusion for purpose of discussion is substantiated. The work sought to characterize changes in analytical precision attributed to differing concentrations through evaluation of fifty-five (55) samples via four analytical methods utilizing two techniques – ICP-AES and XRF. XRF methods focused on major elements on fused glass discs and trace elements in powder pellets, whereas ICP-AES dealt with major elements after fusion decomposition and trace elements, with selected majors after acid digestion.[94] The digestion solution consisted of a hydrofluoric acid [HF] constituent to promote metals liberation from silicate materials to minimize XRF total metals bias. Chromium was the only interference element to prevent reliable precision attributed to low recovery via ICP-AES due to chromite insolubility or chromyl fluoride losses due to HF dissolution.[95] Results indicate that significant precision changes as a function of concentration occurred in 50% of sample population and although XRF is a capable technique, it

> *…cannot compete with ICP-AES used in conjunction with the acid attack sample preparation scheme in terms of the speed and cost with which an extended range of elements can be determined, particularly if a simultaneous is available for use.*[96]

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[93] Michael H. Ramsey, et al., "An objective assessment of analytical method precision: comparison of ICP-AES and XRF for the analysis of silicate rocks", *Chemical Geology,* 124, (1995). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 01/19/08)

[94] Ibid

[95] Ibid

[96] Ibid

Upon cursory review, the following appears to be IH-centric; however further analysis reinforces classification as geological/mining, due to the sample site location(s) and focus on lead silicate matrices. Sixty-eight (68) air samples obtained at various locations within two mill sites processing galena[97] ore were collected on mixed cellulose ester filters and analyses was performed in accordance with NIOSH Methods 7702 and 7701 respectively for portable-XRF and UE/ASV, with FAAS utilized as confirmatory analysis per Method 7082 with and without acid digestion.[98] FPXRF analysis was performed by a Niton Model XL 701 Thin Sample Analyzer calibrated upon start-up, every 10th sample and preceding shutdown. Analytical results illustrate FPXRF yields positive bias compared to the FAAS-acid digestion reference method and is likely attributed to insolubility of lead silicates in the digestion solution and XRFs capability to efficiently analyze them. Since portable-XRF method shows a +26.5% bias over the FAAS-acid digestion reference, it, unlike UE/ASV, does not meet NIOSH accuracy criteria.[99] Drake, et al., concluded that although FPXRF does not meet NIOSH accuracy requirements, it remains an effective screening method for airborne lead provided the user understands matrix dependent overestimation capabilities.

3.1.6 Industrial Hygiene

Traditional occupational exposure assessment performed by an Industrial Hygienist (IH) for any target analyte is essentially a two-step process involving sample collection and analysis. Obtaining representative samples involves differing sample

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[97] a soft lead-gray, very heavy, crystalline mineral, lead sulfide [PbS], with a bright metallic luster, that is the chief ore of lead.

[98] Pamela L Drake, et al., "Evaluation of two portable lead-monitoring methods at mining sites", *Journal of Hazardous Materials,* 102, (2003). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 04/16/08).

[99] Ibid

collection protocols specific to the matrices of interest. Employee inhalation exposure to metal(s) particulate matter (PM) will likely employ personal or area sampling, in which a pump is utilized to pull air through a sample train (located in the worker's breathing zone) consisting of filtration media that entraps the PM and prevents it from entering the pump system. Wipe samples on predetermined surface areas may also be utilized to collect workplace exposure data indicative of possible dermal and inhalation exposure conditions. Thirdly, bulk samples such as soil, sludge, solids, raw materials and a number of other forms may be collected for determining potential exposures from source materials. Regardless of the sample collection means, downstream, off-site analysis at an accredited analytical laboratory is deemed requisite for effective quantification and IH exposure determination. Though the practice is widely accepted as standard today, analytical laboratory analysis requires chain-of-custody documentation, sample transport, utilization of analytical reagents and most importantly, turnaround times ranging from days to weeks. All the while, employee exposure to a potentially hazardous situation may continue until the lab report is received and interpreted by the IH. The following two case studies illustrate how FPXRF may be used to minimize employee exposure during the lag phase between sample collection and receipt of analytical yields.

Funded by the US Department of Housing and Urban Development (HUD), Missouri Department of Health and Centers for Disease Control and Prevention (CDC), Sterling, et al., conducted a comparative evaluation between FPXRF and FAAS for lead dust wipe analysis.[100] The work was performed in response to the fact that the environmental lead laboratory accreditation programs do not include composite sample

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[100] D.A. Sterling, et al., "A Portable X-Ray Fluorescence Instrument for Analyzing Dust Wipe Samples for Lead: Evaluation and Field Samples", *Environmental Research, Section A,* 83, (2000). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 04/16/08).

analysis in their accreditation criteria and compositing is a common method to reduce lab costs, thus:

> *It is, therefore important that reliable, cost-effective, and timely on-site methods be developed for sampling surfaces to confirm levels of lead contamination for screening, risk assessment, elevated blood lead investigations, and abatement/intervention clearance purposes. Additionally, on-site analysis allows for immediate feedback for corrective actions and health education for occupants and workers.*[101]

The researchers employed NITON Model 300 or 700 series units designed for prescreening samples prior to external laboratory analysis. Samples were collected over a two-year period from urban dwellings and also rural homes in proximity to a lead mining operation. In-situ analysis consisted of four separate measurements of 60s duration for each wipe sample, which were then submitted for FAAS analysis following digestion. Quantification limits for FAAS and FPXRF were 25 μg and 20 μg respectively.[102] Supported by the findings of both Shrivastava, et al., and Pérez-Agantegui, et al., Sterling concludes the coefficient of variation (CV) declines as lead [Pb] content increases and precision increases with higher lead content.[103] Interestingly, the work specifies XRF may be more reliable than traditional acid-digestion laboratory techniques because of its ability to determine total metals content versus only acid-labile constituents. Limiting conditions of the FPXRF involved uniform dust distribution and the presence of lead-based paint chips in the wipe sample. The former warrants no further explanation; however visible paint chips on the wipe sample presents two issues;

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[101] Ibid
[102] Ibid
[103] Ibid

first, lead [Pb] may be enclosed within or behind non-lead paint, thus shielding occurs, and; second, leaded paint chips may be oriented in low-response areas of the sampling window, thus yielding a lower reading. Overall, the research concludes that, provided paint chip interferences and detection limits are understood, FPXRF is a viable, in-situ, lead-wipe analytical technique for identification and quantification purposes.[104]

Nygren's work regarding FPXRF application in the industrial hygiene arena addresses occupational exposure to metals and also focuses on the tangible employee benefits attributed to timely analytical feedback versus methodology acceptance and viability. Comparing in-situ, non-destructive XRF to AAS, ICP-AES and ICP-MS, the latter are destructive analytical techniques also incapable of compound speciation, yet require a much greater time period to obtain similar results. Five (5), air filter cassette samples obtained from employee sampling were analyzed via a Niton XRF 700 series instrument operated in the 'thin samples' mode for a total of four-times per sample. Results indicate that in pre-study, AAS produced a lower detection limit and standard deviation over FPXRF.[105] Wipe samples, analyzed three-times each via XRF were within acceptable agreement with a 'spiked' standards sample for cobalt [Co], copper [Cu] and manganese [Mn] and within reasonable agreement for molybdenum [Mo], nickel [Ni], lead [Pb] and platinum [Pt].[106] In an interesting exemplification regarding bulk samples, portable XRF was also utilized as an inspection tool at a window factory to prevent chromated copper, arsenate (CCA) treated wood, which is banned in Sweden for

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[104] Ibid

[105] Olle Nygren, "New approaches for assessment of occupational exposure to metals using on-site measurements", *Journal of Environmental Monitoring,* 4, (2002). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 04/16/08).

[106] Ibid

use in windows, from being introduced into the factory.[107] The most interesting aspect of the work was the positive role FPXRF serves in instantaneously evaluating work task changes aimed at improving working environments.

3.1.7 Scrap Materials

The application of FPXRF in the scrap materials sorting and processing arenas is a logical fit due to in-situ capabilities and the need only for qualitative versus quantitative data. Typically, in scrap metal facilities, identification of the primary material class (aluminum, copper, stainless steel, lead, brass, titanium, steel, cast iron, solder, tin, etc.) is desired instead of actual alloy determination. Though more sophisticated facilities may sort by actual alloy type, the main purpose is that of a screening tool. Research also indicates that portable-XRF is readily employed in the scrap wood industry to sort CCA impregnated wood scrap from non-treated feedstock.

Japanese researchers utilized a Niton XLt 999W FPXRF to evaluate the instruments capabilities to determine steel alloy compositions underlying an external paint layer and concluded on-site screening as a viable application.[108] Difficulties arose in the characterization of certain steel alloying elements as cobalt [Co] was not detected, even in non-coated samples. Researchers attribute this to the fact that both [Co] and nickel [Ni] overlap iron [Fe] spectral lines and the evaluated instrument lacked insufficient resolution to differentiate.[109] In line with other work, researchers reported an exponential decrease in steel alloy elemental signal intensity as paint thickness increased,

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[107] Ibid

[108] Hiroyuki Ida, et al., "Analysis of painted steel by a hand-held X-ray fluorescence spectrometer", *Spectrochimica Acta Part B,* 60, (2005). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 01/12/08).

[109] Ibid

thus surface coating interferences must be considered in FPXRF applications. In another Japanese study evaluating FPXRF for forensic science applications, researchers focused on the shielding effects to determine if packaged contents could be effectively analyzed. Results were similar – an exponential decrease in fluorescent intensity occurs as a function of increasing shield thickness.[110] Thus, although FPXRF may have viable applications in bare metallic scrap materials identification, equipment limitations must be understood for evaluation of coated materials.

In a study performed by University of Miami and University of Florida researchers, the viability of FPXRF for identification of arsenic [As] in CCA treated wood was evaluated. Samples were analyzed in triplicate for 6 seconds each as typical CCA treated wood arsenic levels are 2,000 – 20,000 mg/kg, thus additional acquisition time is unnecessary for precision purposes.[111] However, for samples exhibiting low arsenic concentrations, increased acquisition time should be considered as researchers determined a <1 mg/kg detection limit (DL) over a 10 minute analysis as compared to 9.8 mg/kg for a 6 second acquisition. Comparative analysis between FPXRF and AA techniques illustrates that although yields were not comparable – XRF results were 1.5 – 2.3 times greater - they were correlated and allowed for conversion equations to estimate AA yields from FPXRF data.[112]

In furtherance of the aforementioned arsenic evaluation by FPXRF, two of the four original researchers and their respective peers, evaluated the viability of portable

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[110] Hiroyuki Ida and Jun Kawai. "Analysis of wrapped or cases object by a hand-held X-ray fluorescence spectrometer", *Forensic Science International,* 2-3, (2005). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 04/14/08).

[111] Colleen N Block, et al.,, "Use of handheld X-ray fluorescence spectrometry units for identification of arsenic in treated wood", *Environmental Pollution,* 148, (2007). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 01/08/08)

[112] Ibid

XRF as an effective sorting method of waterborne CCA treated wood scrap in response to arsenic contaminated mulch being sold in retail stores. Since CCA phase-out, new formulations, excluding borate-treatment, are primarily copper-based, thus previously utilized 1-(2-pyridylazo)-2-napthol (PAN) stain for copper detection can no longer differentiate preservative type[113] and an arsenic-specific stain requires 45 minutes reaction time.[114] Therefore, FPXRF efficacy was evaluated to differentiate between CCA-treated and copper-treated wood and in doing so, cost models processing facilities could utilize to estimate sorting costs were developed. Jacobi, et al., determined that commingled waste sorting should be supported with XRF, however manual efforts in doing so are cost-prohibitive, so focus should be made on automated XRF-enhanced sorts.[115]

3.2 FPXRF Capabilities

FPXRF provides a suitable and prompt means of screening predominant contaminants and possesses the requisite characteristics to potentially supplant many traditional laboratory analytical methods of greater cost and turnaround time. Throughout research progression, a spreadsheet clearly delineating both capabilities and limitations of FPXRF as a viable screening tool for RCRA metals has been maintained – the capabilities follow.

Firstly, FPXRF has been accepted by many professional disciplines including geologists, archaeologists, industrial hygienists and EH&S specialists. It has been used

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[113] Gary Jacobi, et al., "Evaluation methods for sorting CCA-treated wood", *Waste Management,* 27, (2007). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 01/08/08)

[114] Colleen N Block, et al.,, "Use of handheld X-ray fluorescence spectrometry units for identification of arsenic in treated wood", *Environmental Pollution,* 148, (2007). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 01/08/08)

[115] Ibid

in lead-paint testing since the 1970s[116], in emergency response applications, cultural pieces authentication and as a characterization tool at remedial sites. Though the majority of reviewed sources tout PXRF as a cost-effective technique, which it appears to be, none substantiated these claims with supporting data comparing a FPXRF versus standard laboratory analytical procedure (SLAP) per sample costs.

Secondly, modern portable-XRF equipment is easy to use and operate, thus requiring minimal training and possible licensure, (if isotope-based), to allow a technician level resource to achieve the same quality results required of a scientist prior. Reducing the commitment of upper echelon labor resources allows them to focus on the overall technical and management aspects versus day-to-day operations.

Thirdly, FPXRFs inherent capability to minimize the sample collection and analyses process was a common thread in the literature. Due to in-situ analytical capabilities, the need for actual sample collection is reduced to confirmatory samples, thus sample collection labor, equipment and container costs, as well as chain of custody (CoC) documentation and sample shipments are reduced.[117,118] Sample preparation methodologies are also affected as some protocols may require no preparation, whereas others may dictate homogenization via screening and thin-film sample preparation. Higher resolution contaminant delineation is also supported by FPXRF as more samples may be obtained, thus increasing site sample densities furthers reliability of decisions and avoids missing localized contaminant zones.

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[116] Dennis Kalnicky and Raj Singhvi, "Field portable XRF analysis of environmental samples", *Journal of Hazardous Materials*, 83, no.1-2, (2001). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 01/08/08)

[117] Dennis Kalnicky and Raj Singhvi, "Field portable XRF analysis of environmental samples", *Journal of Hazardous Materials*, 83, no.1-2, (2001). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 01/08/08)

[118] Puneet Shrivastava, Scott O'Connell and Allen Whitley PhD. "Handheld X-ray Fluorescence: Practical Application as a Screening Tool to Detect the Presence of Environmentally-Sensitive Substances in Electronic Equipment", *ISEE 2005,* pp.157-162

Fourth, the portability of FPXRF allows one to bring the lab to the sample and not the sample to the lab, thus providing environmental benefit by reducing impacts associated with sample transport and also elimination of potentially hazardous laboratory waste. Additionally, in refinery and chemical facility maintenance operations, the ability to field verify materials and prepare replacement parts without requiring process shutdown pays huge dividends. Portability also reduces damage and security risk in cultural study evaluations as one-of-a-kind, invaluable pieces no longer require packaging and transport to a laboratory for FPXRF capable-analysis.

Fifth, FPXRF is a non-destructive technique capable of conducting simultaneous multi-element sample analysis in near real-time. Non-destructive analytical techniques are specifically useful in archaeological applications where the sample integrity must be preserved and also in instances where confirmation via laboratory analysis is required since the original sample remains intact. Multi-element capability is beneficial in that it allows for characterization of non-target analytes that may not have been considered for standard laboratory analysis, but are important to understand for various reasons. Precious metal content in [Pb] contaminated metal hydroxide sludge (EPA waste code F006) is a key example as likely only the RCRA eight metals would have been identified, yet the waste material could have significant monetary value. The rapid analytical turnaround provided by FPXRF was another common literature thread spanning remediation, scrap wood processing and industrial hygiene concepts. Remedial site managers can make extent of contamination decisions much more quickly, wood processors rely on the pass/fail application for CCA sorting and industrial hygienists have expedited access to exposure data, allowing operational or engineering control changes in significantly lesser time than laboratory analyses would support.

FPXRF instrumentation and methodology exhibits considerable distinct benefits and also some drawbacks evaluated against traditional laboratory analytical protocols. Compared to standard nitric acid digestion methods, data gathered by XRF are derived from all matrix materials and thus represents a "total" analysis compared to only acid-labile components.[119] Though the majority of FPXRF readings do not directly correspond with conventional laboratory methods such as inductively conductive plasma-atomic emission spectroscopy (ICP-AES), atomic absorption spectroscopy (AAS) or neutron activation analysis (NAA), the yields are often linear and can be converted to reasonable estimates of anticipated results. [120,121]

3.3 FPXRF Limitations

Like other analytical instrumentation, FPXRF also has limiting characteristics which must be addressed. Firstly, literature indicates portable XRF, regardless if isotope or tube-based, is positively biased to standard laboratory methods utilizing acid digestion and analysis. FPXRF yields a total metals analysis, whereas laboratory procedures may experience digestion and extraction losses or some elements (metal silicates) may not be labile in utilized digestion solutions. This is supported by the findings of both Killbride and Shrivastava, which report FPXRF overestimated cadmium concentrations in samples

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[119] Xiandeng Hou and Bradley T. Jones, "Field instrumentation in spectroscopy", *Microchemical Journal*, 66, no. 1-3 , (2000). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 01/03/08).

[120] Colleen N Block, et al.,, "Use of handheld X-ray fluorescence spectrometry units for identification of arsenic in treated wood", *Environmental Pollution,* 148, (2007). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 01/08/08)

[121] Christian Mans and others, "Development of suitable plastic standards for X-ray fluorescence analysis", *Spectrochimica Acta Part B: Atomic Spectroscopy*, 62, no.2, (2007). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 01/03/08).

containing low levels of the element.[122,123] Additionally, Ramsey concluded a chromium precision bias exists between FPXRF and ICP-AES due to low recoveries in the latter caused by chromite residue or chromyl fluoride losses.[124] Most FPXRF devices also do not have the capabilities to determine lithium [Li], beryllium [Be] or boron [B] as they are considered light metals.

Secondly, quantification of select elements via FPXRF may not be possible, even with high-resolution semiconductor detectors, due to spectral-overlap interference. The most prominent example is the arsenic-lead (As $K\alpha$ / Pb $K\alpha$) overlap in which the US EPA states that [As] cannot be effectively determined in samples with a Pb:As ratio greater than 10:1.[125,126,127,128] Theoretically, this means that a sample containing 500 mg/kg [Pb] would make it difficult to detect [As] at 50 mg/kg, thus arsenic becomes a limiting analyte in samples containing both elements. In their work governing painted steel, Ida et al., reported difficulties in the detection of both cobalt and nickel due to Co $K\alpha$ / Fe $K\beta$ and Ni $K\alpha$ / Fe $K\beta$ overlaps respectively.[129] FPXRF chromium analysis

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[122] J. Pérez-Arantegui, et al., "Characterization of pigments found in traditional Valencian ceramics by means of laser ablation-inductively coupled plasma mass spectrometry and portable X-ray fluorescence spectrometry", *Talanta,* 74, 2008. http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 04/18/08)

[123] Puneet Shrivastava, Scott O'Connell and Allen Whitley PhD. "Handheld X-ray Fluorescence: Practical Application as a Screening Tool to Detect the Presence of Environmentally-Sensitive Substances in Electronic Equipment", *ISEE 2005,* pp. 157-162

[124] Michael H. Ramsey, et al., "An objective assessment of analytical method precision: comparison of ICP-AES and XRF for the analysis of silicate rocks", *Chemical Geology,* 124, (1995). http://library.rit.edu/electronic/scidirect/scidirect.html, (Aaccessed 01/19/08)

[125] Dennis Kalnicky and Raj Singhvi, "Field portable XRF analysis of environmental samples", *Journal of Hazardous Materials*, 83, no.1-2, (2001). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 01/08/08)

[126] J. Pérez-Arantegui, et al., "Characterization of pigments found in traditional Valencian ceramics by means of laser ablation-inductively coupled plasma mass spectrometry and portable X-ray fluorescence spectrometry", *Talanta,* 74, 2008. http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 04/18/08)

[127] M.B. Bernick, et al., "Results of field-portable X-ray fluorescence analysis of metal contaminants in soil and sediment", *Journal of Hazardous Materials*, 43, (1995). http://library.rit.edu/electronic/scidirect/scidirect.html, (Aaccessed 04/19/08)

[128] J. Pérez-Aranetgui, et al., "Characterization of pigments found in traditional Valencian ceramics by means of laser ablation-inductively coupled plasma mass spectrometry and portable X-ray fluorescence spectrometry", *Talanta,* 74, 2008. http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 04/18/08)

[129] Hiroyuki Ida, et al., "Analysis of painted steel by a hand-held X-ray fluorescence spectrometer", *Spectrochimica Acta Part B,* 60, (2005). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 01/12/08).

difficulties due to high detection limits and X-ray interferences caused by moisture and particle size distribution were also reported by Ramsey.[130]

Other major factors influencing FPXRF yields include penetration depth, matrix effects, element concentration, source distance, shielding effects, sample moisture content and sample preparation. Though numerous other possible contributory factors exist, the aforementioned were repeated throughout various sources. Research did not yield a consistent portable XRF penetration depth as values ranged from ~2mm in soils to 2 mm – 90 mm in electronic components to a few μm to mm in ceramics.[131,132,133] Physical matrix effects, including particle size distribution, homogeneity, surface geometry, will vary from in-situ sample to in-situ sample and should be closely watched to ensure they are not a source of FPXRF bias. Target element(s) concentration of the analyzed sample also plays a key role in FPXRF analysis as both Sterling and Block report increased precision with higher element levels.[134,135] The distance from the XRF/detector source to the target sample directly impacts analytical yields as sample concentrations decrease in response to increased separation distance. Thus, it is imperative standard protocol(s) be employed to minimize variances in sample distance which may impact overall results. Shielding effects are similar to sampling distances as

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[130] Michael H. Ramsey, et al., "An objective assessment of analytical method precision: comparison of ICP-AES and XRF for the analysis of silicate rocks", *Chemical Geology,* 124, (1995). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 01/19/08)

[131] Dennis Kalnicky and Raj Singhvi, "Field portable XRF analysis of environmental samples", *Journal of Hazardous Materials*, 83, no.1-2, (2001). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 01/08/08)

[132] Puneet Shrivastava, Scott O'Connell and Allen Whitley PhD. "Handheld X-ray Fluorescence: Practical Application as a Screening Tool to Detect the Presence of Environmentally-Sensitive Substances in Electronic Equipment", *ISEE 2005,* pp. 157-162

[133] J. Pérez-Arantegui, et al., "Characterization of pigments found in traditional Valencian ceramics by means of laser ablation-inductively coupled plasma mass spectrometry and portable X-ray fluorescence spectrometry", *Talanta,* 74, 2008. http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 04/18/08)

[134] D.A. Sterling, et al., "A Portable X-Ray Fluorescence Instrument for Analyzing Dust Wipe Samples for Lead: Evaluation and Field Samples", *Environmental Research, Section A,* 83, (2000). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 04/16/08).

[135] Colleen N Block, et al.,, "Use of handheld X-ray fluorescence spectrometry units for identification of arsenic in treated wood", *Environmental Pollution,* 148, (2007). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 01/08/08)

increased thickness of a painted surface or protective coating functions analogously to increased source distance. Ida's works governing painted steel and objects encased in differing shielding materials indicate decreasing fluoresced x-ray signal intensity in response to increased shield thickness.[136, 137] Moisture content was also identified as a influencing factor effecting portable-XRF yields and it was generally reported that >20% moisture may detrimentally impact analysis. Finally, sample preparation, although partially addressed by the prior subsets thereof, is likely the most critical aspect to ensuring representative and repeatable FPXRF analysis. Instrument users must understand FPXRF is not the 'point and shoot' analytical answer it is often marketed to be and some work may be required to adequately prepare samples for proper analysis. This may include partial removal of a painted surface finish on toy jewelry to characterize the substrate material or separation of plastic components by color type prior to grinding and sieving. The list continues, however the key point is higher homogeneity produces better results.

FPXRF techniques are considerably less sensitive than standard laboratory analytical procedures for quantification purposes as their DLs are higher. However, for qualitative screening applications involving major contaminants, they function quite well. Although Block, et al., reports XRF yields 1.5 – 2.3 times higher than traditional

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[136] Hiroyuki Ida, et al., "Analysis of painted steel by a hand-held X-ray fluorescence spectrometer", *Spectrochimica Acta Part B,* 60, (2005). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 01/12/08).

[137] Hiroyuki Ida and Jun Kawai. "Analysis of wrapped or cases object by a hand-held X-ray fluorescence spectrometer", *Forensic Science International,* 2-3, (2005). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 04/14/08).

laboratory AA, she also reports high correlation, thus supporting conversion equation development to estimate AA values from XRF yields.[138]

Two other potential FPXRF drawbacks are the stigma associated with radiation devices and lack of representative SRMs. Isotope-based hand-held devices will be equipped with one or multiple radioisotopes and therefore require registration by the Nuclear Regulatory Agency (NRC) and corresponding state agencies. Unlike tube-based XRF, isotope-equipped units' house continuously radioactive source(s), which over time must be replaced. Thus procurement of new sources and disposal of those depleted must be considered under increasingly stringent post 9/11 requirements due to 'dirty bomb' potentials. Operator exposure monitoring may also be required and is source dependent. Tube-based units do not fall under NRC jurisdiction, but may be governed by state-specific requirements. In New York, tube-based FPXRF is exempt from registration requirements; however in New Hampshire, it is not.[139] The absence of representative SRMs is considered an impediment by some utilizing FPXRF quantitatively, however for screening purposes these impacts are not as great.

3.4 Summary

This review illustrates that FPXRF has been widely used and accepted by academic, environmental and regulatory communities for identification, qualification and often quantification of certain heavy metals contained in varying environmental samples and could equivocally serve a similar role in evaluation of consumer goods. Noteworthy

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[138] Colleen N Block, et al.,, "Use of handheld X-ray fluorescence spectrometry units for identification of arsenic in treated wood", *Environmental Pollution,* 148, (2007). http://library.rit.edu/electronic/scidirect/scidirect.html, (Accessed 01/08/08)

[139] Per author's EHS employment duties managing multiple northeast US facilities.

is the fact that of the eight RCRA metals, substantiated data regarding mercury, silver and selenium was absent in all works. FPXRF exhibited benefits appear to outweigh the potential limitations as screening tool - the application of which requires a lesser degree of certainty than definitive quantification. It is not anticipated to replace the need for all standard laboratory methods, but instead expedite decisions and quell the number of unnecessary contract laboratory analyses. Attributed to FPXRF acceptance and success per the aforementioned applications, it is logical to surmise assessment of consumer goods would mirror the same results due to pass-fail versus actual analyte quantification.

Methodology

4.1 FPXRF Selection Parameters[140]

Selection of tube-based FPXRF equipment requires an understanding of the principles of X-ray fluorescence spectrometry and knowing the device's potential applications in order to differentiate between requisite versus optional capabilities. Specifying the right device for one's unique application(s) and budget requires careful attention to detail and consideration of the equipment objectives. Factors, including but not limited to, spot diameter, battery-life, communications interfaces, weight, operating modes, ergonomics, accessories, cost, limits of detection (LOD), and NEMA ratings must all be evaluated.

Spot diameter refers to the analyzable area of a sample in which incident X-rays will be directed and therefore fluoresced. Prior to 3mm small-spot devices entering the market, typical FPXRF ranges were 8 – 60 mm. Small spot devices are advantageous as they allow for analysis of minute components without potential cross-contamination from surrounding regions.

Powering of FPXRF devices is accomplished either via AC power or multi-cell Li-ion battery packs, although some may still utilize Ni-Cd sources. Published run times range from 6 – 12 hours, with 8 hours the nominal. Factors which should be considered include the number of batteries included with purchase, replacement costs, charging time, reduced battery life in cold weather conditions and disposal restrictions.

FPXRF units collect and store analytical data which requires eventual extraction, by means of personal computer, so it may be formatted, stored or shared. Connectivity

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[140] Data obtained from author's personal work experience in FPXRF procurement

and transfer is accomplished either through PDA, hard-line serial or USB ports or wirelessly via Bluetooth^{TM} technology. Combined with manufacturer-integrated management software, the data download and manipulation portion can be as simple as ‘drag-and-drop’ or may require exclusivity within the software application portal.

Compared to legacy, radioisotope-based FPXRF units, which were often rectangular in shape and held in the palm of the hand, today’s tube-based units are of a cushioned pistol-grip design that provides better ergonomics leading to decreased operator fatigue. Additionally, device mass continues to decline with typical weights ranging from 2.5 – 4.0 lbs. Ruggedized, weather-proof units (NEMA 3) may be slightly heavier; however of those researched, none exceeded 5.0 pounds.

Many of the FPRXF units available today are pre-programmed with specific operating modes which allow for faster analytical cycles based on the matrix of interest. Common modes of operation include: alloy (metallurgy, electronics/solder and precious metals); bulk (soil, mining); plastic (halogens and metals in consumer goods); EU RoHS (Br, Cd, Pb, Cr, Hg); RCRA metals; lead paint; and thin film.

Current tube-based FPXRF units operate at approximately 100 times less power than common X-ray equipment found in a dentist’s office. Silver [Ag], tungsten [W] or gold [Au] are the prevalent anode materials of construction utilized to yield tube voltages ranging from 10 – 50 kV; with 40 kV being the most common upper limit. Lower voltage units (10 – 25 kV) typically employ Ag anodes, whereas those rated at 50 kV utilize Au. The unwritten tube-based FPXRF rule-of-thumb regarding scalable X-ray power is ‘more is better’ as it allows for greater sample excitation in less time, thus increasing device operating efficiency and reducing ROI.

Understanding tube-based FPXRF limits of detection (LOD) can be daunting task as published values are often matrix-specific, thus accepting at face value without consideration for one's own applications may lead to selection of an incorrect instrument. Common applications listed by device manufacturers include EU RoHS compliance, mining/geology, scrap processing, lead-paint analysis and environmental sampling; however the potential is virtually limitless. Defining requisite LODs is a two-phased process which first requires specifying the device objectives as either qualitative, quantitative (concentration) or both, then determining analyte-specific desired detection limits. Table 4.0, recreated from a FPXRF manufacturer's product literature, illustrates common elements LODs, based on 60 – 120 second sample events of matrices ranging from 5% iron (Fe) to silicon dioxide (SiO_2).[141]

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[141] http://www.innovx.com/products/literature. (Accessed 10/03/08). Document ID# 29-2-E, Pg.8.

Table 4.0

FPXRF LODs

Element	LOD (ppm)
Antimony (Sb)	30-50
Arsenic (As)	7-10
Barium	150-200
Cadmium (Cd)	15-20
Chromium (Cr)	30-50
Copper (Cu)	15-20
Lead (Pb)	10-15
Mercury (Hg)	10-15
Nickel (Ni)	20-25
Selenium (Se)	7-10
Silver (Ag)	15-20
Thallium (Tl)	10-15
Tin (Sn)	30-50
Zinc (Zn)	15-20

Typical tube-based FPXRF prices range from \$25,000 - \$60,000 and vary in accordance with equipment configuration and functionality. Available integrated options - all of which increase base unit costs - include Bluetooth™ wireless, RFID reader/writer, touch-screen display, digital camera, bar code scanner and even GPS for sample point data-logging. Additional accessories designed to complement FPXRF equipment use include soil boots for environmental analysis, high-capacity battery packs, field-holsters, power adapter kits for international applications, hot-surface adapters, weld isolation masks and stationary test stands.

The tube-based FPXRF device utilized in this research was a Niton XL3t 700, graciously loaned from Thermo Scientific of Billerica, MA.

4.2 Sample Selection Parameters

Infants/children's products and toy samples shall meet the following criteria for research inclusion:

- Intended for use by children 0 – 7 years of age
- Limited to non-wearable items (costume jewelry excluded)
- Samples shall be of type and geometry that allows direct mouthing
- Samples shall cost less than five-dollars ($5.00) per unit
- Samples shall consist of differing matrices, including one sample set each of plastic, rubber, wood, metal, plated/coated product and bulk (modeling clay, crayons, chalk)

4.3 Contract Analytical Laboratory Selection

Adirondack Environmental Services, Inc. (AES), located at 314 North Pearl St in Albany, NY 12207 (http://www.adirondackenvironmental.com/) was chosen to perform the total and TCLP metals analyses. AES holds the following accreditations/certifications and was well-qualified to satisfy the applicable analytical requirements of this research.

- America Industrial Hygiene Association (AIHA)
- National Environmental Laboratory Accreditation Program (NELAP)

- National Voluntary Laboratory Accreditation Program (NVLAP)
- New York State Department of Health ELAP
- Commonwealth of Massachusetts Department of Environmental Protection
- State of Connecticut Department of Public Health
- State of Pennsylvania Registered Laboratory
- USDA Soil Permit

4.4 Sample Lot Storage

All samples were photographed and assigned discrete identifiers, based on matrix type prefixes (PLAS = plastic, RUBB = rubber, META = metal, WOOD = wood, COAT = plated or coated and BULK = bulk) and number/component within the sample set. Thus, PLAS-001-A represents the "A" component in the plastic matrix set. Purchased samples were not removed from original packaging and resided in labeled, re-sealable type plastic bags accommodative of sample geometry until one-hour prior to preparation and analyses. Storage conditions were of ambient temperature (70^{o}F +/-2^{o}) and humidity (30 - 35%) representative of an average household with samples residing in a closed "tote" type container typically used to store household items and children's toys.

4.5 Sample Preparation

Preparation of test samples was minimized to mimic the actual conditions infants/children's products or toys undergo from point-of-purchase to point-of-use. One-hour prior to tube-based FPXRF analysis, the samples were removed from the storage "tote" and re-sealable plastic bag, extracted from their packaging and prepared for tube-based FPXRF analysis. All samples underwent size-reduction as necessary for accommodation in the tube-based FPXRF test-stand chamber. Due to the instrument's ability to differentiate substrate material from surface coatings, samples were not subjected to segregation of plating/coating from the substrate for independent analysis.

Since FPXRF is a non-destructive analytical method, analyzed samples were placed in labeled, re-sealable plastic bags and stored prior to courier pick-up by the contract analytical laboratory, Adirondack Environmental Services (AES). Relinquished samples were subsequently prepared by AES in accordance with specified test protocols and methodologies.

4.6 FPXRF Analysis Protocol

Per manufacturer recommendations, the instrument was calibrated to a resolution <220 eV prior to sample analyses and operated in the *Consumer Goods/Test All* mode. Analysis via this mode of operation allows the instrument to determine the best methodology via fundamental parameters theory and minimizes the potential for improper manual sample matrix selection by the operator. In essence, it's considered the 'foolproof' method for analysis of consumer products, which could consist on unknown or multiple matrices. Each sample was placed in the stationary test stand and analyzed three-times for 120 seconds each with the results averaged to yield the reported value (See Table 6.0). Due to sample geometries, small-spot diameter and thin-film analyses were deemed unnecessary and thus were not performed.

4.7 Total Metals Analysis Protocol

Total metals or “totals analysis” was performed by Adirondack Environmental Services in accordance with SW-846 and functioned as a preliminary screening analysis to determine the need for further TCLP if the ‘totals metal’ yield was twenty-times (20x) greater than the TCLP regulatory limit. Samples were shipped on April 7, 2009 and results received April 17, 2009. Mercury was prepared and analyzed in accordance with SW7471A, whereas all remaining analytes were prepared in accordance to SW3050B and analyzed by inductively coupled plasma (ICP) per SW6010B.

4.8 TCLP Protocol

Although a total metals lead (Pb) yield of 253 ppm for sample COAT-001-B exceeded the 20x TCLP regulatory limit multiplier (100 ppm), a TCLP was not performed due to the lack of adequate & viable sample volume subsequent to the total metals analyses.

Results

Tables 5.0 - 6.0 below illustrate the reported yields in parts per million (ppm) for each utilized analytical methodology

5.1 FPXRF Screening

Rubber was the only analyzed matrix in which all of the RCRA metals were non-detect (ND) as all others had a positive yield for one or more analytes. Barium and chromium were the commonly detected substances at 50% incidence, whereas arsenic, cadmium, mercury and selenium were not detected in any matrices above the instrument's limit(s) of detection (LOD).

Table 5.0

FPXRF Analytical Yields

Sample ID#	Arsenic (ppm)	Barium (ppm)	Cadmium (ppm)	Chromium (ppm)	Lead (ppm)	Mercury (ppm)	Selenium (ppm)	Silver (ppm)
PLAS-001	ND	**231**	ND	**43**	**160**	ND	ND	ND
RUBB-001	ND	ND	ND	ND	ND	ND	ND	ND
META-001	ND	ND	ND	**190,767**	ND	ND	ND	ND
WOOD-001-D	ND	**285**	ND	ND	ND	ND	ND	ND
COAT-001-B	ND	ND	ND	**415**	**2095**	ND	ND	**1108**
BULK-001-B	ND	**2427**	ND	ND	ND	ND	ND	ND

5.2 “Totals” Analysis

Compared to initial FPXRF Screening results in Table 6.0, there were no matrices which yielded complete ND values for the eight (8) analytes. Barium incidence levels increased with total metals analysis to ~83%, whereas chromium remained stable at 50% detection. Arsenic, mercury, selenium and cadmium yields were very similar to FPXRF screening results, excluding one Cd yield above LOD at 1.01 ppm.

Table 6.0

Total Metals Analytical Yields

Sample ID#	Arsenic (ppm)	Barium (ppm)	Cadmium (ppm)	Chromium (ppm)	Lead (ppm)	Mercury (ppm)	Selenium (ppm)	Silver (ppm)
PLAS-001	ND	25.6	**1.01**	**3.68**	**22**	ND	ND	ND
RUBB-001	ND	1.22	ND	ND	ND	ND	**0.254**	ND
META-001	ND	ND	ND	**42.1**	ND	ND	ND	ND
WOOD-001-D	ND	**140**	ND	ND	**2.03**	ND	**1.14**	ND
COAT-001-B	ND	**211**	ND	**43.3**	**_253*_**	ND	ND	ND
BULK-001-B	ND	**542**	ND	ND	ND	ND	**0.348**	ND

* indicates yield which was greater than 20x the TCLP regulatory limit

Analysis & Discussion

Detailed review of the analytical yields obtained via both FPXRF and total metals methodologies illustrates considerable variability between the two. Thus, for comparative analysis purposes, the data was viewed on an analyte-specific basis versus matrix type. Following are the research findings and a brief discussion of each.

Arsenic (As) and mercury (Hg) yielded non-detectable (ND) concentrations for both performed methodologies, therefore correlation may be assumed although no detectable amounts were present in any of the six (6) sample matrices.

Barium (Ba) was detected above the LOD 50% of the time with FPXRF and 83% via total metals analysis, thus making it the highest incidence analyte of the eight. The RUBB-001 and COAT-001-B matrices resulted in ND concentrations via FPXRF, but yielded 1.22 ppm and 211 ppm respectively for total metals analysis. This difference is believed to be attributed solely to the XRF instrument's 150 – 200 ppm LOD for barium, whereas the totals analysis has a much lower LOD to provide quantitative yields at or below FPXRFs capabilities. In the remaining sample sets, the FPXRF readings ranged ~100% - 350% higher for WOOD-001-D and BULK-001-B matrices than totals analysis; however for PLAS-001, the inverse was true as a totals result of 231 ppm was witnessed compared to the 25.6 ppm FPXRF value. The higher yields in the WOOD matrix could be attributed to the limited sample area of the FPXRF compared to the entire sample volume utilized in total metals analyses which may have contributed to overall barium concentration dilution. Limited sample area could also explain the PLAS total metals yield being greater than FPXRF due to the sample spot containing lesser barium than the overall sample. For BULK analysis, the higher FPXRF yield is not believed to be attributed to sample homogeneity, but instead availability of accessible, non-encapsulated barium within the crayon matrix for acid dissolution.

Excluding the PLAS-001 sample for totals analysis, both methodologies recorded non-detectable (ND) concentrations of cadmium (Cd) across all matrices, therefore correlation is assumed although no discernible presence was witnessed. The difference between the 1.01 ppm totals yield and ND FPXRF result was simply a matter of the latter's LOD being 15-20 times greater than the actual totals value.

The chromium (Cr) analyte presented the most perplexing results of the research due to the extremely high concentration variability between FPXRF and totals analysis on the META-001 sample set. Detectable values were witnessed across the plastic, coating and metal matrices with variability ranging from 858% - 1068% on the former two; however the totals vs. FPXRF yield on the latter was 190,767 ppm versus 42.1 ppm, yielding an enormous 453,000% difference. In Ramsey's work comparing FPXRF to ICP-AES in silicate rocks, it was discovered that chromite insolubility or chromyl fluoride losses due to HF dissolution resulted in significant low recovery via ICP-AES compared to the total chromium yield produced by FPXRF. Although the META matrix chromium was not anticipated to be in silicate form, it follows along in principle that the digestion solution may have been inadequately robust for chromium liberation. This is further supported by the fact that the chemical industry often utilizes 316 stainless steel materials for containerization and storage of nitric acid compounds.

Excluding ND results and instances in which the totals analytical yield was below the FPXRF LOD, the FPXRF instrument consistently yielded higher concentration values, ranging from 627% - 728%, for lead (Pb). The greatest XRF yield of 2095 ppm however only resulted in a 253 ppm total metals yield - which should be mentioned was a qualified TCLP candidate, but remaining sample volume was insufficient to perform the analysis. The lead (Pb) yields should be considered similar to barium (Ba) in that higher FPXRF results were due to localized analysis versus the entire sample or that the element was matrix-bound and inaccessible to the dissolution compound.

Like cadmium (Cd), the difference between detect and non-detect for the selenium (Se) analyte was simply a matter of lower detection limit capabilities with the totals methodology. Yields of 0.254, 1.14 and 0.348 were well below FPXRFs 7 – 10 LOD capabilities.

Silver (Ag) was detected only once in all sample sets. The 1108 ppm FPXRF yield from COAT-001-B was well above the instrument's 15 – 20 ppm LOD, but did not produce a detectable total metals yield. This is likely due to the FPXRF yielding only a localized area and penetration depth, whereas the totals analysis utilizes the entire sample therefore resulting in analyte dilution.

Conclusions

FPRXF has been widely accepted among many scientific and industrial communities as a viable, cost-effective and time-saving method for in-situ qualitative and/or semi-quantitative/quantitative analysis of multiple environmental and material matrices. This thesis essentially added another category to that repertoire – infants/children's products and toys.

Research indicated that FPXRF is a potentially viable screening tool for RCRA metals in infants/children's products and toys, but regulatory definitions and device limitations must be clearly understood when evaluating compliance. For instance, samples must be delineated for either *homogenous material* or *article* analysis as the latter may lead to target analyte dilution and possibly erroneous compliance certification. Whereas the converse may result in an article being tagged as non-conforming due solely to a homogenous material analysis. Thus, it is critical to define objectives and parameters prior to engaging in any analytical activity, especially instances of homogenous materials versus articles as overall yields may be orders of magnitude in difference.

Additionally, FPXRF provides a matrix-dependent, 'point-in-time yield' of a relatively small area which may or may not be representative of even a homogenous sample composition and certainly not representative of complex articles. Thus, to rectify homogenous material differences, it is suggested that a statistically significant number of readings be obtained from numerous locations on the sample and averaged accordingly to yield a mean value. Complex articles however, such as a laptop computer, present a much more difficult task as the article may be comprised of tens to hundreds of homogenous materials, many of which may be embedded or encapsulated within the unit.

In instances such as this, one would be required to first know the number of homogenous materials, their locations and volume or mass, then isolate them in order to effectively analyze and estimate overall chemical composition. The process would likely be extremely laborious, rife with errors and cost prohibitive compared to the ROI of a total metals analysis. Thus, for articles analysis, increasing complexity equates to less desirability for FPXRF utilization.

Furthermore, FPXRF provides a total analyte reading compared to traditional wet-lab dissolution labile substances, thus one must anticipate a higher yield and interpret accordingly. This holds especially true in certain matrices where target analyte encapsulation may occur (sintered glass, crystal, colored concrete, etc.); therefore additional FPXRF sample preparation steps such as homogenization via crushing, sieving and/or pelletizing may be necessary. It is also important to ensure the target analyte is labile to the digestion compound utilized by the lab for the requested analysis to ensure maximum dissolution – this may require significant enough changes to standard methods that the laboratory may charge for 'custom' analysis.

Finally, analyte spectral interferences such as arsenic/lead (As/Pb) and nickel/cobalt/iron (Ni/Co/Fe) may result in false-positive or negative yields, thus detailed understanding of sample matrices and equipment capabilities is required prior to analysis. The issue of FPXRF resolution due to spectral overlap is best left to the equipment manufacturers whom will hopefully soon develop a solution for differentiating these interferences. However, in the interim and solely for alloys, the materials-savvy researcher may be able to implement alternate methodologies to extrapolate empirical data which will allow for informed decision-making based on analysis of common ‘alternative analytes’. For instance, a 60/40 Sn/Pb solder joint may not yield a viable lead (Pb) concentration due to arsenic (As) contamination, but focusing on the tin (Sn) concentration may help narrow down the specific prospects. The same is true for stainless steel (SS) affected by the Ni/Co/Fe overlaps via knowledge that SS contains chromium (Cr) in differing concentrations per alloy type. The last circumvent methodology for metals identification due to spectra overlap is to target the major alloying constituent in order estimate the material classification (copper, aluminum, magnesium, titanium, etc) and hone-in via minor constituent yields.

Although the research did not produce viable data to determine FPXRF efficacy to effectively predict RCRA hazardous waste metal(s) toxicity characteristics, conclusions may still be drawn from the total metals yields and lessons learned conveyed. Since FPXRF tends to overestimate total metals, caution must be utilized as a qualifying screening tool for downstream TCLP analysis otherwise costly, unwarranted analyses could arise. Additionally, FPXRF screening should incorporate multiple sample locations in effort to determine analyte homogeneity versus localization prior to performing total metals or TCLP analysis. Finally, matrix consideration and wet-lab methodologies must always be taken into account as certain materials may exhibit significantly different compositions between analytical methodologies, (e.g. – META chromium yields). In retrospect, perhaps the research should have utilized matrix-specific certified controls of known or spiked composition to compare FPXRF, total metals and TCLP yields. However, this approach was neither cost-feasible nor would it have represented real-world instances of infants/children’s products and toys.

In the global product compliance realm, product stewardship responsibilities are often flowed down to the organization's environmental, health and safety (EHS) departments as these are the individuals often deemed best-qualified due to their education and knowledge of chemical substances and product safety. Intersection between EHS product stewardship roles and FPXRF occurs when a downstream user or consumer advocacy group utilizes FPXRF as a 'point-and-shoot' tool for product conformity assessments without truly understanding its capabilities and limitations. From the author's personal experience, the results may be claims of non-conformity based on improperly prepared or analyzed samples yielding erroneous data. Therefore EHS professionals must have a rudimentary understanding of FPXRF principles in order to objectively evaluate data and provide an informed response.

Appendix A

Product Name	Recall Date	Units Recalled	Classification	Country of Mfg.	Recall Hazard
Blobo Plastic Bubb-A-Loons	12/7/1976	15,000,000	Toys	Taiwan	Benzene
Bed Guard Rails	1/4/1977	Unknown	Infant/Child Products	Not Specified	Lead
Snoopy Toy Bank	9/12/1977	60,000	Toys	USA	Lead
ABC Educational Blocks	12/8/1977	8,400	Toys	Taiwan	Lead
Products for Blind Children	10/3/1977	Unknown	Infant/Child Products	USA	Lead
Stuffed Toys	8/25/1978	500,000	Toys	South Korea	Lead
FIBRO-CLAY Modeling Compound	3/1/1983	Unknown	Infant/Child Products	USA	Asbestos
Stuffed Baby Chicks, Ducks & Goslings	4/13/1983	25,000	Toys	China	Arsenic
Stuffed Chicks & Ducklings	4/20/1984	150	Toys	China	Arsenic
Danara Baby Crib Exercisers	12/5/1985	100,000	Infant/Child Products	Not Specified	Lead
Woodworks Lace Up Horse	3/24/1986	550	Toys	Taiwan	Lead
Play Brooms	8/28/1986	100,000	Infant/Child Products	Hungary	Lead
Voltron Lion Robot Sets	11/12/1986	203,000	Toys	Taiwan	Lead
Voltron Lion - Deluxe Lion	11/12/1986	424,000	Toys	Taiwan	Lead
Voltron Lion -Miniature Lions	11/12/1986	866,000	Toys	Taiwan	Lead
Children's Wooden/Straw Chairs	2/11/1987	9,000	Infant/Child Products	Mexico	Lead
Toy Train	3/24/1987	900	Toys	Taiwan	Lead
Toy Chest Music Box	3/24/1987	900	Toys	Taiwan	Lead
Musical Mobile Crib	6/4/1987	364	Toys	USA	Lead
Wooden Painted Puzzles	11/25/1987	400	Toys	Mexico	Lead
Water Toys & Squeaking Toy Snake	7/14/1988	8,000	Toys	Hong Kong	Lead
Baby Guards Hand Holders	8/4/1988	20,000	Infant/Child Products	Not Specified	Lead
Color In Contrast Busy Boxes	6/26/1989	40,000	Toys	Not Specified	Lead
Slinky Pull Toys	11/21/1989	Unknown	Toys	USA	Lead
Music Maker Elephant Toys	3/29/1990	750	Toys	China	Lead
Bo-Bo Pacifiers	4/2/1990	20,000	Infant/Child Products	Hong Kong	Nitrosamines
Jumpin Jeans Denim Paint Kits	5/22/1991	700,000	Infant/Child Products	Not Specified	Lead
Little Tikes Crib Centers	6/16/1992	16,300	Toys	USA	Lead
Childrens Puzzles	3/4/1993	10,000	Toys	Israel	Lead
Children's Carry-All Bags	4/2/1993	650,000	Infant/Child Products	Not Specified	Lead
Children's Necklaces/Bracelets	12/13/1993	65,000	Infant/Child Products	China	Lead
Crayons	3/22/1994	430	Toys	China	Lead

Crayons	4/5/1994	965,585	Toys	China	Lead
Product Name	**Recall Date**	**Units Recalled**	**Classification**	**Country of Mfg.**	**Recall Hazard**
Animal Shape Wagons	5/6/1994	1,000	Toys	China	Lead
Wooden Armadillos	5/6/1994	5,000	Toys	Mexico	Lead
Scented Teether	7/19/1994	9,000	Infant/Child Products	China	Toxic, irritant scent
Kaleidoscope Art Sets - Crayons	9/7/1994	14,000	Toys	China	Lead
Magic Diamond Paper Weight	7/28/1995	864	Toys	Taiwan	Petroleum distillates
Liquid Water Timers	7/28/1995	1,800	Toys	Taiwan	Ethylene Glycol
Wooden Armadillos & Turtles	4/2/1996	42,000	Toys	Mexico	Lead
Little Wood Wagon	10/12/1996	14,000	Toys	Not Specified	Lead
Plastic Halloween Bucket	10/24/1996	11,700	Toys	China	Lead
Exploring Nature science Activity Kit	11/26/1996	34,000	Toys	Not Specified	Kerosene
Wooden Toys	12/17/1996	44,400	Toys	China	Lead
Paperweights & Pens	12/17/1996	40,000	Infant/Child Products	Not Specified	Petroleum distillates
Necklaces	5/12/1997	4,800	Infant/Child Products	Not Specified	Lead
Children's Umbrellas	8/5/1997	6,500	Infant/Child Products	Not Specified	Lead
Wee Patsy Travel Set	1/29/1998	2,500	Toys	Not Specified	Lead
Halloween Floating Eyeballs	4/8/1998	329,000	Toys	Taiwan	Kerosene
Smiley Face Floating Balls	4/8/1998	100,000	Toys	Taiwan	Kerosene
Tweety Water Timer Game Key Rings	4/8/1998	2,500	Toys	Not Specified	Ethylene Glycol
Payless Novelty Purses	5/18/1998	6,000	Toys	China	Petroleum distillates
Oscar Mayer Weinermobile Pedal Car	6/2/1998	16,000	Toys	Not Specified	Lead
Bubble Beauties	6/8/1998	500	Toys	China	Petroleum distillates
Mulan Backpacks	8/18/1998	3,700	Infant/Child Products	Not Specified	Lead
Mulan Rolling Luggage	8/18/1998	1,800	Infant/Child Products	Not Specified	Lead
Children's Furniture	9/3/1998	8,300	Infant/Child Products	Not Specified	Lead
Magnet Games	12/21/1999	21,000	Toys	Taiwan	Lead
Children's Picnic Sets	6/1/2000	1,200	Toys	Not Specified	Lead
Barbie Sunglasses	2/21/2001	70,000	Toys	China	Petroleum distillates
Ti-Dee Helper Child's Broom	3/1/2001	2,200	Toys	Mexico	Lead
Educational Kits	3/1/2001	13,000	Toys	Not Specified	Lead
Galileo Weather Thermometer	6/19/2001	28,000	Toys	China	Flammable liquid
Kitty Kitty Kittens	7/10/2001	238,000	Toys	China	Contaminated Water
Velcro Wallets	7/10/2001	55,000	Infant/Child Products	China	Lead

Educational Kits	7/10/2001	160,000	Infant/Child Products	Not Specified	Lead
Product Name	**Recall Date**	**Units Recalled**	**Classification**	**Country of Mfg.**	**Recall Hazard**
Dollhouse Furniture Sets	8/20/2001	10,000	Toys	China	Lead
Powerscout Sterling Teething Ring	1/10/2002	200	Infant/Child Products	Not Specified	Solder flux
Pedal Cars	2/20/2002	75,000	Toys	Korea	Lead
Harry Potter Key Chain	4/18/2002	7,000	Infant/Child Products	Not Specified	Petroleum distillates
Chicago Bears Bobblehead Figurines	9/17/2002	100,000	Toys	China	Lead
Lamaze Activity Toys	4/4/2003	3,800	Toys	Not Specified	Lead
Toy Necklace	10/10/2003	1,400,000	Toys	India	Lead
Multicolored Sidewalk Chalk	11/13/2003	26,000	Infant/Child Products	Hong Kong	Lead
Multicolored Sidewalk Chalk	11/24/2003	50,000	Infant/Child Products	Hong Kong	Lead
Lily Pad Clacker Instrument	1/14/2004	430	Toys	India	Lead
Discovery Kids Pottery Wheel Kits	1/26/2004	150	Toys	China	Bacteriological
Children's Rings	3/2/2004	1,000,000	Toys	India	Lead
Dread Pirate Coffee Table Game	5/24/2004	2,000	Toys	China	Lead
Metal Toy Jewelry Intended for Vending Machines	7/8/2004	150,000,000	Toys	Not Specified	Lead
Children's Furniture Set	8/19/2004	3,800	Infant/Child Products	China	Lead
Children's Jewelry	12/17/2004	155,000	Infant/Child Products	China	Lead
Children's Costume Bracelets	1/11/2005	7,100	Toys	China	Lead
Toddler Drinking Cups	2/17/2005	720	Infant/Child Products	China	Petroleum distillates
Nu-Tronix Karaoke Cassette Player/Recorder	4/13/2005	220,000	Toys	China	Lead
Zebco Children's Fishing Products	4/13/2005	1,500,000	Toys	China	Lead
Metal Heart-Shaped Pendants	5/12/2005	80,000	Infant/Child Products	China	Lead
Shakespeare Children's Fishing Kits	6/17/2005	438,000	Toys	China	Lead
Children's Watches	8/17/2005	50,400	Infant/Child Products	China	Petroleum distillates
Maptangle World Edition Floor Mat MaP	8/25/2005	140	Toys	Taiwan	Lead
Children's Sunglasses	9/1/2005	12,900	Infant/Child Products	Taiwan	Lead
Disney Princess Bracelet Keyrings	9/22/2005	145,000	Infant/Child Products	China	Lead
Necklace & Earring Sets	9/22/2005	455,000	Infant/Child Products	China	Lead
Children's Cribs	11/22/2005	335	Infant/Child Products	Indonesia	Lead
Metal Necklaces & Zipper Pulls	11/30/2005	6,000,000	Infant/Child Products	China	Lead
Art Accentz™ Changlz™ Metal Charms	2/23/2006	29,000	Infant/Child Products	China	Lead
Glowin' Dino & Glowin' Doggy Flashlights	3/1/2006	20,800	Toys	China	Lead
Metal Charm Bracelets	3/23/2006	25,000	Infant/Child Products	China	Lead

Necklace & Ring Sets	3/23/2006	580,000	Infant/Child Products	China	Lead
Product Name	**Recall Date**	**Units Recalled**	**Classification**	**Country of Mfg.**	**Recall Hazard**
Reebok Charm Bracelet	3/23/2006	300,000	Infant/Child Products	China	Lead
American Girl Children's Jewelry	3/30/2006	180,000	Toys	China	Lead
Children's Necklaces	4/27/2006	55,000	Infant/Child Products	China	Lead
Metal Charm (DVD Inserts)	5/5/2006	730,000	Infant/Child Products	China	Lead
Juicy Couture Children's Jewelry	5/10/2006	2,800	Infant/Child Products	China	Lead
Bendable Dog & Cat Toys	8/17/2006	340,000	Toys	China	Lead
Cars Toy Storage Benches	11/9/2006	3,000	Infant/Child Products	China	Lead
Children's Mood & Diva Necklaces	12/4/2006	51,600	Infant/Child Products	China	Lead
Children's Butterfly Necklaces	12/13/2006	29,000	Infant/Child Products	China	Lead
Powerpuff Necklaces	12/13/2006	48,000	Infant/Child Products	China	Lead
Gigantic Gemstone Ring	12/19/2006	194,000	Infant/Child Products	China	Lead
Butterfly Necklaces	1/18/2007	113,800	Infant/Child Products	China	Lead
Children's "Rachael Rose Kidz" Rings	2/7/2007	280,000	Infant/Child Products	China	Lead
Children's "Ultra Gear" Bracelets	2/7/2007	86,400	Infant/Child Products	China	Lead
Children's "Kidsite" Necklace and Earring Sets	2/23/2007	6,000	Infant/Child Products	China	Lead
"Claudia Jublot" Children's Rings	2/23/2007	115,000	Infant/Child Products	China	Lead
Elite 5-in-1 Easels	3/7/2007	2,500	Infant/Child Products	China	Lead
Mood Necklaces	3/13/2007	3,600	Infant/Child Products	China	Lead
Elite Operations Toys Sets	3/13/2007	128,700	Toys	China	Lead
Children's Necklaces	3/15/2007	58,000	Infant/Child Products	China	Lead
Children's Mood Necklaces	3/15/2007	47,000	Infant/Child Products	China	Lead
Stuffed Fun Balls	3/28/2007	7,200	Toys	China	Lead
Children's "Groovy Grabber" Bracelets	4/3/2007	4,000,000	Infant/Child Products	China	Lead
Metal Key Chains	4/3/2007	396,000	Infant/Child Products	China	Lead
Charm Bracelets & Necklaces	4/17/2007	900,000	Infant/Child Products	India	Lead
Children's Religious Fish Necklaces	5/2/2007	132,000	Infant/Child Products	China	Lead
Children's Rings with Dice or Horseshoes	5/2/2007	200	Infant/Child Products	India	Lead
Anima Bamboo Collection Games	5/2/2007	5,000	Toys	China	Lead
Children's Necklaces, Bracelets and Rings	5/15/2007	200,000	Infant/Child Products	China	Lead
Children's Turquoise Rings	5/15/2007	300,000	Infant/Child Products	China	Lead
Budding Gardener Complete Gardening Set	5/16/2007	80	Infant/Child Products	China	Lead
Invincibles Transport Converters Toy Sets	5/23/2007	3,000	Toys	Hong Kong	Lead

Eli's Small Drum & Liberty's Large Drums	5/30/2007	4,500	Toys	China	Lead
Product Name	**Recall Date**	**Units Recalled**	**Classification**	**Country of Mfg.**	**Recall Hazard**
Thomas & Friend Wooden Railway Toys	6/13/2007	1,500,000	Toys	China	Lead
Butterfly Necklaces	6/19/2007	19,000	Infant/Child Products	China	Lead
Essentials for Kids Jewelry Sets	7/5/2007	20,000	Infant/Child Products	China	Lead
Sleeping Beauty Crown and Cinderella Star Earring Sets	7/17/2007	220	Infant/Child Products	China	Lead
Soldier Bear Brand Toy Sets	7/18/2007	13,000	Toys	Hong Kong	Lead
Sesame Street, Dora the Explorer, etc	8/2/2007	967,000	Toys	China	Lead
Sarge Die Cast Cars	8/14/2007	253,000	Toys	China	Lead
Magnetic Toy Train Sets	8/21/2007	27,000	Toys	China	Lead
Spinning Tops	8/22/2007	66,000	Toys	China	Lead
Tin Pails	8/22/2007	4,700	Toys	China	Lead
TOBY & ME Jewelry Sets	8/22/2007	14,000	Infant/Child Products	China	Lead
Children's Divine Inspiration Charm Bracelets	8/22/2007	7,900	Infant/Child Products	China	Lead
SpongeBob SquarePants™ Address Books and Journals	8/22/2007	250,000	Infant/Child Products	China	Lead
Robbie Ducky Kids Watering Can	8/28/2007	6,000	Infant/Child Products	China	Lead
Imaginarium Wooden Coloring Cases	8/30/2007	27,000	Infant/Child Products	China	Lead
Geo Trax Locomotive Toys	9/4/2007	90,000	Toys	China	Lead
Big Big World 6-in-1 Bongo Band	9/4/2007	8,900	Toys	China	Lead
Barbie Accessory Toys - Various	9/4/2007	675,000	Toys	China	Lead
Floor Puppet Theaters	9/26/2007	10,000	Toys	China	Lead
Children's Toy Rake	9/26/2007	16,000	Toys	China	Lead
Britain's Knights of the Sword Toys	9/26/2007	800	Toys	China	Lead
Happy Giddy Gardening Tools & Sunny Patch Chairs	9/26/2007	350,000	Toys	China	Lead
Thomas & Friend Wooden Railway Toys	9/26/2007	200,000	Toys	China	Lead
Children's Spinning Wheel-Metal Necklaces	9/26/2007	850	Infant/Child Products	China	Lead
TOBY & ME Jewelry Sets	9/26/2007	23,500	Infant/Child Products	China	Lead
Frankenstein Tumblers	10/4/2007	63,000	Infant/Child Products	China	Lead
Key Chains	10/4/2007	192,000	Infant/Child Products	China	Lead
Bookmarks & Journals	10/4/2007	150,000	Infant/Child Products	China	Lead
Childrens Toy Decorating Sets	10/4/2007	15,000	Toys	China	Lead
Pirates of Caribbean Medallion Squeeze Lights	10/4/2007	79,000	Toys	China	Lead
Baby Einstein Color Blocks	10/4/2007	35,000	Toys	China	Lead
Wooden Toys	10/4/2007	10,000	Toys	China	Lead

Cub Scouts Totem Badges	10/9/2007	1,600,000	Infant/Child Products	China	Lead
Product Name	**Recall Date**	**Units Recalled**	**Classification**	**Country of Mfg.**	**Recall Hazard**
Disney Deluxe Winnie-the-Pooh 23 pc Play Set	10/11/2007	49,000	Toys	China	Lead
Princess Magnetic Travel Art Set Lap Desk	10/11/2007	7,800	Infant/Child Products	China	Lead
Bendable Dinosaur Toys	10/11/2007	10,000	Toys	China	Lead
Deluxe Wood Art Sets	10/11/2007	19,000	Infant/Child Products	Taiwan/Vietnam	Lead
Kidnastics Balance Beams	10/11/2007	2,400	Infant/Child Products	Taiwan	Lead
Cool Clip & Mini Cool Clip Bookmarks	10/17/2007	200,000	Infant/Child Products	China	Lead
Tabletop Puppet Theaters	10/17/2007	5,400	Infant/Child Products	China	Lead
Halloween Skull Pails	10/17/2007	50,000	Infant/Child Products	China	Lead
WeGlow Children’s Metal Jewelry	10/25/2007	110,000	Infant/Child Products	China	Lead
Beary Cute, Expressions, and Sassy & Chic Metal Jewelry	10/25/2007	198,000	Infant/Child Products	China	Lead
Purple Halloween Pails with Witch Decorations	10/25/2007	142,000	Infant/Child Products	China	Lead
Toy Gardening Tools	10/25/2007	97,000	Toys	China	Lead
Go Diego Go Animal Rescue Boats	10/25/2007	38,000	Toys	China	Lead
Galaxy Warriors Toy Figures	10/31/2007	380,000	Toys	China	Lead
Ugly Teeth Party Favors	10/31/2007	43,000	Infant/Child Products	China	Lead
Elite Operations Toys	10/31/2007	16,000	Toys	China	Lead
Ribbit Board Games	10/31/2007	1,500	Toys	China	Lead
Decorative Packaging - Pearl Like Bead Attachments	11/1/2007	4,000	Infant/Child Products	China	Lead
Pull Back Action Toy Cars	11/7/2007	380,000	Toys	China	Lead
Robot 2000 Tin Collectable	11/7/2007	2,600	Toys	China	Lead
Dizzy Ducks Music Box	11/7/2007	1,300	Toys	China	Lead
Winnie-the-Pooh Spinning Top	11/7/2007	3,600	Toys	China	Lead
Duck Family Collectable Wind Up Toy	11/7/2007	3,500	Toys	China	Lead
Dragster & Funny Car Toy	11/7/2007	7,500	Toys	China	Lead
"Big Red" Wagons	11/7/2007	7,200	Infant/Child Products	China	Lead
Aqua Dots	11/7/2007	4,200,000	Toys	China	GHB
Curious George Plush Doll	11/8/2007	175,000	Toys	China	Lead
Children's Sunglasses	11/8/2007	58,000	Infant/Child Products	China	Lead
Halloween Themed Baskets	11/16/2007	10,000	Infant/Child Products	China	Lead
Rachel Rose and Distinctly Basics Assorted Metal Jewelry	11/16/2007	205,000	Infant/Child Products	China	Lead
Shaving Paint Brushes	11/21/2007	20,000	Infant/Child Products	China	Lead
Crystal Innovations Jewelry	11/21/2007	200,000	Infant/Child Products	China	Lead

La Femme NY Children’s Necklace and Earring Sets	11/21/2007	4,500	Infant/Child Products	China	Lead
Product Name	**Recall Date**	**Units Recalled**	**Classification**	**Country of Mfg.**	**Recall Hazard**
Children’s Metal Necklaces and Bracelets	11/21/2007	10,400	Infant/Child Products	China	Lead
Decorative Stretchable Aqua Bracelets	11/21/2007	45,000	Infant/Child Products	China	Lead
Sparkle City Charm Bracelets and Tack Pin Sets	11/21/2007	43,000	Infant/Child Products	China	Lead
Children’s Pencil Pouches	11/21/2007	84,200	Infant/Child Products	China	Lead
Boppy® Slipcovers	11/21/2007	38,000	Infant/Child Products	China	Lead
Collectable Mini Helmets	12/5/2007	1,400	Toys	China	Lead
First Years 3-in-1 Flush and Sounds Potty Seats	12/6/2007	160,000	Infant/Child Products	China	Lead
Children's Sunglasses	12/7/2007	260,000	Infant/Child Products	China	Lead
Fishing Games	12/12/2007	14,000	Toys	China	Lead
Horseshoe Magnets	12/12/2007	153,000	Infant/Child Products	India	Lead
Codeena Princess Children’s Metal Jewlery	12/13/2007	1,000	Infant/Child Products	China	Lead
Robbie Ducky Holiday Water Globe	12/13/2007	60	Toys	China	Lead
Baby Bead & Wire Toys/Speed Race Pull Back Cars	12/13/2007	300,000	Toys	China	Lead
Giant Measuring Chart	12/19/2007	13,000	Infant/Child Products	China	Lead
Soldier Bear Toys	12/19/2007	11,400	Toys	China	Lead

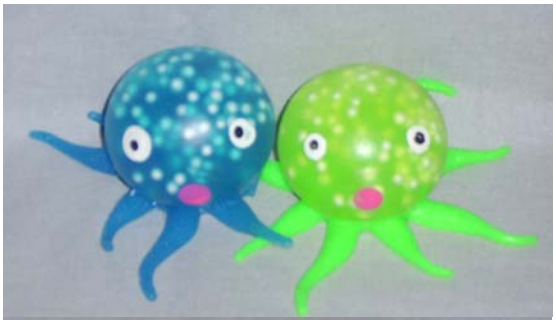
Appendix B

COAT-001-B
(Light Blue Paint)

META-001
(Back of Dogtag)

PLAS-001
(Right Earstem)

RUBB-001
(Blue Tentacles)



WOOD-001-D
(Green Blocks)

BULK-001-B
(Red Crayon)

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15 U.S.C § 1261

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