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Rapid screening of heavy metals and trace elements in environmental samples using portable X-ray fluorescence spectrometer, A comparative study

Jacqueline Q. McComb,

Interdisciplinary Environmental Science Ph.D. Program, Jackson State University, 1400 J.R. Lynch Street, Jackson, MS 39217

Christian Rogers,

Interdisciplinary Environmental Science Ph.D. Program, Jackson State University, 1400 J.R. Lynch Street, Jackson, MS 39217

Fengxiang X. Han, and

Department of Chemistry and Biochemistry and Interdisciplinary Environmental Science Ph.D. Program, Jackson State University, 1400 J.R. Lynch Street, Jackson, MS 39217

Paul B. Tchounwou

Interdisciplinary Environmental Science Ph.D. Program, Jackson State University, 1400 J.R. Lynch Street, Jackson, MS 39217

Abstract

With industrialization, great amounts of trace elements and heavy metals have been excavated and released on the surface of the earth and dissipated into the environments. Rapid screening technology for detecting major and trace elements as well as heavy metals in variety of environmental samples is most desired. The objectives of this study were to determine the detection limits, accuracy, repeatability and efficiency of a X-ray fluorescence spectrometer (Niton XRF analyzer) in comparison with the traditional analytical methods, inductively coupled plasma optical emission spectrometer (ICP-OES) and inductively coupled plasma optical emission spectrometer (ICP-MS) in screening of major and trace elements of environmental samples including estuary soils and sediments, contaminated soils, and biological samples.

XRF is a fast and non-destructive method in measuring the total concentration of multi--elements simultaneously. Contrary to ICP-OES and ICP-MS, XRF analyzer is characterized by the limited preparation required for solid samples, non-destructive analysis, increased total speed and high throughout, the decreased production of hazardous waste and the low running costs as well as multi-elemental determination and portability in the fields. The current comparative study demonstrates that XRF is a good rapid non-destructive method for contaminated soils, sediments and biological samples containing higher concentrations of major and trace elements.

Unfortunately, XRF does not have sensitive detection limits of most major and trace elements as ICP-OES or ICP-MS but it may serve as a rapid screening tool for locating hot spots of uncontaminated field soils and sediments.

1. Introduction

With industrialization, great amounts of trace elements and heavy metals have been excavated and released on the surface of the earth and dissipated into the environments. Trace elements occur in natural environments ubiquitously in small amounts and when present in sufficient bioavailable concentrations, they are toxic to living organisms (Adriano, 2001). They occur as ions compounds, complexes and adsorbed/precipitated/co-precipitated on mineral surfaces. Human activities have drastically altered the biogeochemical cycles and equilibria of these trace metals in the ecosystems. Trace elements enter the ecosystems via direct discharges from industrialization processes, sewage sludge, atmospheric deposits and agricultural practices including application of pesticides or fertilizers (Han et al., 2002, 2003, Han, 2007). They can be transferred from sediments to benthic organisms and then become a potential risk to human consumers through the food chain (Soto-Jiménez et al., 2011).

Widespread increases of trace metals including Cd, Hg, and Pb have been estimated to be on the order of 10–15% since the turn of the century in agricultural soils in Europe (McBride, 1995). Globally World soils have been seriously polluted by Pb and Cd and slightly by Zn (Han et al., 2002). The industrial age anthropogenic Pb, Hg and Cd inputs in the pedosphere are 9.6, 6.1 and 5.2 times those in the lithosphere, respectively. The potential anthropogenic heavy metal inputs in the pedosphere tremendously increased after the 1950s, especially for Cr and Ni. In 2000, the cumulative industrial age anthropogenic global production of Cd, Cr, Cu, Hg, Ni, Pb and Zn was 1.1, 105, 451, 0.64, 36, 235, and 354 million metric tons, respectively.

Traditionally, trace elements and heavy metals in soils and sediments are determined with atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometer (ICP-OES) after acid digestion of the samples. With more convenience and multi-element measurement capability, ICP-OES/ICP-MS have become an attractive instrument for simultaneously determining co-contaminants in environmental samples (Han *et al.*, 2006 etc.). Velitchkova *et al.* (2004) employed an ICP-OES to study spectral interferences in the determination of trace elements in environmental materials. Our previous study showed that mercury measurements in soil and plant samples using ICP-OES were in agreement with those analyzed using ICP-MS and cold vapor atomic absorption spectrometry (CVAAS) analysis (Han *et al.*, 2006). Digestion of soil samples with 4 M HNO₃ and direct measurement by ICP-OES gave a reasonable and acceptable recovery for determining Hg in soils (Han et al., 2006). ICP-OES/ICP-MS gives sensitive detection limits, satisfactory through-out, reliable recovery and accuracy with multi-elements and ICP-MS specifically is capable of measuring isotope ratios of elements (Tseng et al., 1997). All these traditional analytical methods require pre-treatment process of soil and sediment samples with acid digestion. This step is the time consuming process and easily causes the inputs of cross contamination among samples. Moreover, ICM-MS is strongly affected by complex matrix effects. We have developed a rapid measurement procedure for determining mercury in environmental samples by application of a portable total mercury analyzer (Kelly et al., 2012). Our results demonstrated that these three instrumental methods (ICP-OES, CVAA and mercury

analyzer) yielded similar mercury concentrations and statistical data while the mercury direct analyzer had the advantages of not requiring for sample digestion and only requiring a small quantity of samples for distribution of mercury in a single root, a single root hair and sub-regions of a single leaf of plants (Kelly et al., 2012).

X-ray fluorescence spectrometer (XRF) has progressively become an effective method of obtaining high-resolution elemental records because of its non-destructive and nearly continuous measurements. The advanced operating conditions enhance the detection efficiency and improve the minimum detection limits for several elements analyzed (Liang et al., 2012). XRF has been used by geochemists for the past 50 years as a first-order technique to determine the whole-rock chemistry of geological samples. The availability of efficient radioisotope source excitation combined with highly sensitive detectors and wavelength dispersive electronics has initiated the widespread acceptance of XRF technology (Kalnicky and Singhvi, 2001). X-ray fluorescence spectrometry has been established as advantageous when compared to other multi-elemental techniques such as ICP-MS/ICP-OES. The main advantages of XRF analysis are the limited preparation required for solid samples, non-destructive analysis, increased total speed, the decreased production of hazardous waste, the low running costs and portability. Marina and Lopez (2001) used both X-ray fluorescence and ICP-OES to determine phosphorus in raw materials and ceramics and reported similar results. Hannaker et al. (1984) presented a closed agreement of the results of a large number of elements in geological materials (rocks) between XRF and ICP-OES. Kilbride et al. (2006) investigated a comparison study of trace and major elements in soils determined with both X-ray fluorescence and ICP-OES after acid digestion. They found a high degree of linearity between ICP-OES and XRF with X-ray tube for Fe and Pb while for Fe, Cu, Zn, Pb, Cd and Mn between ICP-OES and XRF with the dual source instrument. However, due to the complexity of environmental samples and multi-elements' measurement, there have been a limited comparative studies on their detection limits, accuracy and precision of determination of a variety of trace elements and heavy metals in different environmental samples (contaminated soils/sediments, biological samples and field estuary sediments) with XRF and traditional ICP-OES/ICP-MS.

The objectives of this study are to determine the detection limits, accuracy and precision of XRF for a variety of major and trace elements/heavy metals of environmental concern and to evaluate applicability of XRF in determination of these elements in estuary soils/sediments, contaminated soils and biological samples.

2. Materials and Methods

2.1. Estuary Soil/Sediment Samples

The study area is the Grand Bay National Estuarine Research Reserve (NERRS) which is a part of the 28 U.S. network systems, located in southeastern Mississippi. That includes 18,000 acres of healthy estuarine salt marshes. Soil samples were collected from the Grand Bay NERRS. About 120 sediments samples were collected. The sampling sites are located within the estuary, along the Bayou Heron, Bayou Cumbest, Crooked Bayou, and Bangs Lake. Soil samples were 0 to 5 cm depth. Soil samples were air dried and ground through 120 mesh (stainless steel). A X-ray fluorescence spectrometer (Niton Xlt3) and acid-

digestion/ICP- OES method were used for determining major and trace elements in the samples.

2.2. Contaminated Soils from Oak Ridge, TN

Soil samples from a location near the U.S. Department of Energy Oak Ridge, TN, U.S.A. were obtained previously. The Y-12 National Security Facility near the city of Oak Ridge, Tennessee, USA is a manufacturing and developmental engineering facility that formerly produced components for various nuclear weapons systems. Mercury has been identified as a key contaminant in soil, sediment, surface water, groundwater, buildings, drains, and sumps in the Y-12 watershed (Han et al., 2006). The source of the mercury is from elemental mercury used during the 1950s and early 1960s for the manufacture of nuclear weapons. Mercury was used to capture enriched lithium by separating the lithium isotopes. The estimates of the total mercury released to the environment ranged from about 75 to 150 metric tons (Turner et al., 1985; USEPA, 1989). This soil is Armuchee soil (clayey, mixed, thermic Ochreptic Hapludults). This is a moderately deep soil with a clayey subsoil. Armuchee soils are formed in residuum of shale and river alluvia. The sampling site was located in a floodplain field of the Lower East Fork Poplar Creek (LEFPC) of Oak Ridge, TN. A series of surface soils (0–20 cm) were sampled from both woodland area and wetland/grassland. Soil samples were air dried and ground to pass a 2-mm sieve (Han et al., 2006, 2013).

2.3. Oysters from the Gulf of Mexico

Selected oyster samples were collected (in triplicates) from regional fish markets of the Gulf of Mexico. During the laboratory preparation the soft tissue of oysters were detached from the oyster shell and washed and then boiled in deionized water for 10 minutes -- excess liquid was discarded. The tissue was then transferred to clean watch glasses and dried at 70°C for 48 hours. The dried tissue was pulverized with an agate mortar and pestle then blended (stainless steel, Waring Commercial Blender). The blended tissue (powder) was placed in a desiccator for further analysis.

2.4. Standard Soils

Two certified standard reference soils were used in this study for investigating the accuracy, precision and repeatability of the XRF method (NIST SRM 2710, Montana I soil, Highly Elevated Trace Element Concentrations and NIST SRM 2711a Montana II soil, Moderately Elevated Trace element Concentration).

2.5. Soil Digestion Procedures for ICP-OES and CVAAS

For acid digestions of samples, an environmental express hotblock was implemented in accordance with EPA methods 3050 B. A mixture of H₂O₂/HNO₃ was used to extract major, trace elements and heavy metals from soil/sediment samples. The samples were heated to 95° ± 5°C (hot block) to reflux for 10 to 15 minutes without boiling. Oyster samples were digested in a same manner. ICP-OES was used to measure these elements in digested solutions of all samples and CVAAS was used for measuring mercury concentrations in the samples with low concentrations (Han et al., 2006).

2.6. Reagents

All chemical reagents are trace-metal grade. The concentrated nitric acid and 30% H₂O₂ for the digestion of samples and for matrix-matching of calibration and quality control standards were purchased from Fisher Scientific (Pittsburg, PA). Deionized water (17.8 MΩ-cm) was used for the dilution of samples and standards and was provided by a nanopure infinity ultrapure water system from Barnstead International (Dubuque, IA).

2.7. X-ray Fluorescence Spectrometer (XRF) Instrumentation

A X-ray fluorescence spectrometer (XRF) (Thermo Scientific Niton XL2) was used to determine major and trace elements in soils and sediments and oyster samples. Samples were introduced, via an open-ended sample plastic cell. An acid-purified sand (SiO₂) was used as the media blank for determining the detection limits of major and trace elements and heavy metals. This sand was pretreated with dilute nitric acid overnight and washed with deionized water.

3. Results and Discussion

3.1. Limits of Detection and Limits of Quantification

A high quality of pure quartz has been washed with diluted acid overnight and washed with deionized water and then used to run XRF as blanks. A series of blanks (quartz) were run to determine the limit of detection (LOD) and limits of quantification (LOQ) (Table 1). The LOD can be expressed as the lowest analyte concentration that an instrument can reliably detect (MacDougall et al., 1980). This is the minimum concentration of any element which the method can detect, however, the level of accuracy is greatly decreased. The LOQ can be defined as the level above which quantitative results are acquired with a certain amount of confidence (Keith, et al., 1983). The detection limit can be expressed as the lowest analyte concentration that an instrument can reliably detect (MacDougall *et al.*, 1980, Han *et al.*, 2006, Kelly et al., 2011). In order to calculate the LOD, the standard deviation of blank values was multiplied by three followed by the division of this value by the slope of the calibration curve. Similarly, the LOQ was calculated by multiplying the standard deviation by ten and then dividing this value by the slope of the calibration curve (Skoog *et al.*, 2007). All elements detected with XRF were divided into three categories: major elements (Fe, Mn, Ti, Ca, K, S and Ba), most common trace elements (Mo, Pb, Se, As, Hg, Zn, Cu, Ni, Co, Cr, V, and Cd) and other non common trace elements (Zn, Sr, U, Rb, Th, Au, Sc, Sb, Sn, W, Cs, Te, Ag and Pd). The LOD values calculated for XRF were from 11 to 70 mg/kg for major elements with mostly between 10–20 mg/kg, from 0.61 through 14 mg/kg for most common trace elements with a majority of < 4 mg/kg, and from 0.33 to 30 mg/kg for other uncommon trace elements (Table 1). In general, the values of XRF's detection limits were higher than those with ICP-OES/MS and AAS.

Kalnicky and Singhvi (2001) reported that the detection limits of 22 major and trace elements in a representative sample instead of the blank sample with XRF. The values of detection limits determined with a representative sample were in general larger than the values with a blank sample (quartz sand) in the current study. In addition, we compared calculated detection limits for all these elements with the time of measurement from 2, 5 to

10 min. We found that increasing in measurement time did not improve the detection limits of most these major and trace elements and heavy metals (except for Pb) (data not shown). However, Kalnicky and Singhvi (2001) found the decreasing in the detection limits with increasing the measuring times with a representative samples. Kilbride et al. (2006) also reported that XRF analyzer performance improved with increased analysis time for Cu, Mn and Pb, but not for Fe, Zn, Cd, Ni and As.

3.2. Accuracy and Precision/Reproducibility

The accuracy was determined by testing two certified reference soil standards containing major and trace elements and heavy metals. NIST SRM 2710 (Montana soil) basically contained higher amounts of most trace elements (Cu, Zn, Pb, U, Hg, and Mo et c.) than NIST SRM 2711a (Montana II soil) (Figs. 1 and 2). Five to eight replicates were run on both soils. For both major elements (Fe, Mn, Ti, Ca, and K) and trace elements (Pb, Cr, Rb, Zn, Cu, V, Mo), XRF generated high recoveries of 80%–120% mostly, while the recoveries of As, Hg and U gave the overestimate compared to the certified values (Fig. 3).

To further check the precision and accuracy as well as reproducibility of XRF measurements, the two standard soil samples were examined with three measurements. We calculated relative errors among three measurements for all major and trace elements (Fig. 4). The CV% for all major elements (Fe, Mn, Ti, Ca, K, S) and trace elements (Zr, Pb, Sr, U, Rb, Zn, Cu, V, Hg and Sc) were all below 10%, indicating that XRD achieved a good reproducibility among measurements. However, CV% for Th, Mo and As were in range of 18–28%.

3.3. Application of XRF for Determining Mercury Level in Contaminated Soils

We have applied XRF for determining total mercury levels in mercury contaminated soils from Oak Ridge, TN. Soil samples were surface soil at 0–20 cm from both woodland area and wetland/grassland of a floodplain field, which was located in a floodplain field of the Lower East Fork Poplar Creek (LEFPC) near the US Department of Energy Oak Ridge, TN, USA. This soil is clayey, mixed, thermic Ochreptic Hapludults formed in residuum of shale and river alluvia.

Soils samples were determined directly with XRF and ICP-OES/CVAAS after acid digestion (Han et al., 2006). The results show that XRF gave a reasonable recovery (about 80%) of total mercury in contaminated soils (Fig. 5). The two methods were in much agreement with R^2 0.80 at 5% significant level. The current set of surface soil samples contained the total mercury in the range of 62–316 mg/kg with an average of 145 mg/kg. Previous study indicated that the major mercury form in these floodplain soils was mainly the non-cinnabar mercury (Han et al., 2013), which showed a strong linear relationship with mercury concentrations in native earthworms (both mature and immature groups). Thus, the current study implies that XRF is a good tool for screening mercury hot spots in the floodplain ecosystems of Oak Ridge site.

3.3. Application of XRF in Determining Zinc Level in Oyster Samples

We also applied XRF for measurement of trace elements and heavy metals in biological samples. A series of oyster samples have been sampled from the markets of the Gulf of Mexico. After the samples were dried they were ground with the steel less blenders. The samples were determined with XRF and ICP-OES after acid digestion. Data show that XRF generated good recoveries (106%) of Zn as determined with ICP-OES after acid digestion (Fig. 6). The zinc concentrations in the current oyster samples from the Gulf of Mexico were in the range of 1773 – 12,452 mg/kg with an average of 6,116 mg/kg Zn. Oysters contain high concentration of zinc and good sources of zinc nutrition as well as potential pollution sources of other trace elements and heavy metals. This study showed that XRF is a good tool to rapidly monitor zinc level in oyster samples.

3.5. Application of XRF for Screening Zn and Cu in Estuary Soils and Sediments

We applied XRF to screen both Cu and Zn in 119 estuary soils and sediments from the Grand Bay reserve. A significant high linear relationship was obtained between values of Zn determined with ICP-OES after acid-digestion and direct XRF measurement (R^2 : 0.76 **, n: 119). The total Zn and Cu concentrations in these samples were 0.74–66 mg/kg and 0.12–26 mg/kg with averages of 16 and 8.3 mg/kg, respectively as determined by acid digestion, followed measurement with ICP-OES. Since a significant number of samples were below or near to the detection limits of XRF as determined in this study (2.41 mg/kg), the values detected with XRF only accounted for 66% of those determined with ICP-OES. For Cu, XRF has a poor detection limit (6.52 mg/kg) and Cu levels in a large number of samples were below the detection limit. Thus, the poor linearity was found between the two methods for Cu (Fig. 7). This study shows that XRF provides poor quality data for screening trace elements in uncontaminated fields with low concentrations since most of these elements are present near the detection limits. However, XRF may be a promising screen tool for searching the hot spots of the fields.

4. Conclusions

Contrary to ICP-OES, ICP-MS, CVAAS, X-ray fluorescence spectrometer (XRF) are characterized by the limited preparation required for solid samples, non-destructive analysis, increased total speed, the decreased production of hazardous waste as well as multi-elemental determination. Running samples using XRF is rapid (less than 2 min per sample). XRF has the highest throughput per day, especially for a laboratory with a large amount of samples and it is durable, portable, and cost efficient. It is a good monitoring tool for contaminated soils, sediments and biological samples containing higher concentrations of major and trace elements. Unfortunately, XRF does not have sensitive detection limits for most major and trace elements as ICP-OES/ICP-MS/CVAAS instrumentation. Thus XRF may give a rough estimate for most of trace elements in uncontaminated fields as a good screening tool for hot-spots.

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Fig. 1. Comparisons of major elements measured with XRF and with ICP-OES after acid-digestion for two standard soils.

Fig. 2.
Comparisons of trace elements measured with XRF and with ICP-OES after acid-digestion for two standard soils.

Fig. 3. Recovery (%) of major and trace elements measured with XRF over the standard values for two standard soils.

Fig. 4.
CV% of three measurements of trace and major elements for two standard soils with XRF.

Fig. 5. Comparison of measurements of mercury concentrations in contaminated field Oak Ridge soils with ICP-OES/CVAAS (after acid digestion) and XRF.

Fig. 6. Comparison of concentrations of zinc in oyster samples from the Gulf of Mexico measured with ICP-OES (after acid digestion) and XRF

Fig. 7. Comparison of Zn and Cu in estuary soils and sediments from the Grand Bay Reserve determined with XRF and ICP-OES after acid digestion.

The limits of detection (LOD) and limits of quantification (LOQ) of selected major elements and trace elements determined with XRF in a quart sample (10 min) (mg/kg)

Major Elements														
	Fe	Mn	Ti	Ca	K	S	Ba							
LOD	12.4	19.4	11.6	17.8	37.2	33.0	68.2							
LOQ	41.2	64.6	38.8	59.4	124	110	227							
Most Common Trace Elements														
	Mo	Pb	Se	As	Hg	Zn	Cu	Ni	Co	Cr	V	Cd		
LOD	1.20	0.70	0.73	0.61	2.39	2.41	6.52	14.4	9.01	14.06	2.82	4.35		
LOQ	3.99	2.34	2.44	2.04	7.95	8.03	21.7	48.0	30.0	46.9	9.39	14.5		
Other Trace Elements														
	Zr	Sr	U	Rb	Th	Au	Sc	Sb	Sn	W	Cs	Te	Ag	Pd
LOD	0.96	0.33	0.94	0.35	0.74	1.58	0.85	9.77	6.01	7.25	17.2	29.4	2.99	2.52
LOQ	3.2	1.1	3.1	1.2	2.5	5.3	2.8	32.6	20.0	24.2	57.5	98.1	10.0	8.4