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Evaluation of portable XRF instrumentation for assessing potential environmental exposure to toxic elements

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ABSTRACT

Portable instruments based on X-Ray Fluorescence Spectrometry (XRF) have the potential to assist in field-based studies, provided that the data produced are reliable. In this study, we evaluate the performance of two different types of XRF instrument (XOS prototype and Thermo Niton XL3t). These two XRF analysers were evaluated in a laboratory setting, and data were reported for 17 elements (As, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Sn, Sr, Ti, V, and Zn). Samples analysed ($n = 38$) included ethnic herbal medicine products (HMPs), ethnic spices (ES), and cosmetic products (CPs). Comparison analyses were carried out using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). In general, results reported for Cd, Cu, and Pb by the XOS prototype analyser, using the non-metal mode, were negatively biased (5–95%) as compared to ICP-OES. In contrast, results reported for Pb, As, Cd, Cu and Zn by the Niton, using the soil mode, were positively biased, in some instances (Cd) by up to four orders of magnitude. While the sensitivity of both instruments was insufficient for reliably 'quantifying' toxic elements below 15 mg/kg, XRF was still capable of positively 'detecting' many elements at the low single-digit mg/kg levels. For semi-quantification estimates of contaminants at higher levels, and with limited sample preparation, both XRF instruments were deemed fit for the purpose. This study demonstrates that modern XRF instrumentation is valuable for characterising the elemental content of food, cosmetic, and medicinal products. The technology is particularly useful for rapidly screening large numbers of products (100's per day) in the field, and quickly identifying those that may contain potentially hazardous levels of toxic elements. Toxic elements can be confirmed by examining the raw spectrum, and the limitations of factory-based calibration are generally manageable for field-based studies.

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Supplemental data for this article can be accessed at.

1. Introduction

Public health agencies traditionally rely on an analytical laboratory to support their investigations of human exposure to heavy metals. Such laboratories are typically accredited to national or international standards, and use certified methods of analysis that require a high level of skill and training. For the major toxic elements Pb, Cd, Hg, and As, approved (or official) methods typically mean those based on Inductively Coupled Plasma Mass Spectrometry (ICP-MS), ICP-Optical Emission Spectrometry (OES), and/or Atomic Absorption Spectrometry (AAS). These 'destructive' methods require that the sample should be usually digested prior to analysis, and are both time-consuming, relatively expensive, and required significant technical skills.

For public health investigations, the advantages of non-destructive, portable technologies are clearly obvious, especially for field-based investigations where the turn-around time and low-cost per analysis is important. For example, use of Ayurvedic medicines among immigrants from the Indian subcontinent, and the wide spread use of traditional herbal medicine products (HMPs) among Chinese communities, represents a growing concern from a public health perspective. The World Health Organization (WHO) estimates that 70–80% of the population in developed countries has utilised some form of alternative or complementary treatment, while up to 80% of the population in some African and Asian countries rely on traditional medicine for primary health care [1].

In the United States, HMPs are widely available and while some may be regulated as drugs, others may be considered dietary supplements. Furthermore, the use of alternative therapies is often unsupervised by either a medical doctor or a practitioner of alternative medicine [2]. While HMPs may be considered as 'natural' and therefore they may be interpreted as having low risk of harm, the reality is that little is known about the chemical content of HMPs. Potential safety concerns related to the use of HMPs include undeclared ingredients such as prescription drugs, interactions with conventional medicines, and contamination with heavy metals [3,4]. Indeed, some studies have reported detecting one or more toxic metals or metalloids up to weight per cent levels in some Ayurvedic products [5]. Metals may be intentionally incorporated into traditional medicines, such as in the *rasa shastra* practice of Ayurveda, where the 'equilibrium' of elements such as Hg, Pb, and Zn is considered essential for the normal functioning of the human body. However, potential sources of contamination for other HMPs include use of agricultural pesticides (e.g. lead arsenate), growing plant raw materials in polluted soil, and poor manufacturing controls such as use of metal-grinding apparatus or storage container [6,7]. HMPs and other ethnic products may constitute a significant and preventable source of exposure to toxic elements, so characterising their elemental content is important for monitoring the human environment and in protecting public health.

Recent studies have reported on specific elements in HMPs using methods such as AAS or ICP-OES [7,8,9,10,11,12], while others have reported data based on X-Ray Fluorescence Spectrometry (XRF) methods [13,14,15,16]. The XRF-based approaches are generally non-destructive, rapid, and require limited sample preparation compared with AAS or ICP-OES, and they are also relatively inexpensive. In addition, the availability of portable XRF instrumentation offers the potential for rapid trace element

determination in HMPs and similar products under field conditions [17,18] such as in a subject's home or at a port of entry. Thus, XRF has the potential to facilitate rapid identification of potentially toxic products. However, correct use of portable XRF instrumentation requires some understanding of XRF, the sample being analysed, the element being measured, and, more importantly, the limitations of the technology. Comprehensive reviews of XRF and its application to food, biological, and commercial product samples are available from Atomic Spectrometry Updates, and are published annually [19].

The development of new technologies that can be used to assess potential personal environmental exposure either at home or in the work place creates new possibilities for exposure assessment studies. Such efforts have been supported in the USA by the National Institutes of Health (NIH) as part of the agency's The Genes, Environment and Health Initiative (GEI) [20]. In particular, the NIH effort is focused on exposure biology, and the need to develop new technologies for assessing environmental exposure to individuals [21].

In response to these needs, new XRF instrumentation based on doubly curved crystal (DCC) enabled monochromatic X-Ray Optic Technology (M-XRF) was developed by X-Ray Optical Systems, Inc. (XOS, East Greenbush) with NIH support. According to XOS, DCC optics has the potential to increase the sensitivity of XRF and improve performance at low levels [22]. With NIH support, a prototype M-XRF instrument, which was initially called the 'Personal Environmental Analyzer' (PEA), was assembled by XOS. The prototype XOS analyser was designed to measure a wide range of elements in liquids, gels, or solid sample types, including HMPs, personal care products, food, beverages, etc. It was envisioned that the analyser would enable individual environmental exposure assessments to be conducted in the home, place of employment, or in a recreational setting with little or no sample preparation required.

The principal goal of this study was to evaluate the analytical performance of the XOS prototype analyser in the laboratory, including its accuracy, precision, limits of detection, and possible interferences, and to report on the feasibility for field-based studies. The XOS prototype analyser was compared to a commercial handheld XRF instrument, the Niton XL3t (Thermo Scientific, Tewksbury, MA), which is also used for elemental screening of samples collected from the personal environment. Analytical performance for both instruments was assessed using HMPs, ES, and CP for up to 17 elements, including As, Ba, Cd, Cr, Co, Cu, Fe, Hg, Mn, Ni, Pb, Se, Sr, Sn, Ti, V, Zn. The XRF data, obtained using factory-based algorithms and/or specific calibration modes, were compared to independent values obtained by ICP-OES following acid digestion.

2. Experimental

2.1. *Certified reference materials*

A variety of certified reference materials (CRMs) were analysed on the XOS prototype analyser and on the Niton. The CRMs were selected based on specific elements present, with a certified elemental content >1 mg/kg. An effort was made to obtain CRMs with a variety of matrices that might be encountered in the personal environment. CRMs included National Institute of Standards and Technology (NIST) Standard Reference

Material (SRM) 1547 Peach Leaves (NIST, Gaithersburg, MD), Institute of Reference Materials and Metrology (IRMM, Geel, Belgium) BCR 627 Tuna Fish Tissue, National Research Council (NRC, Ottawa, Canada) DORM-2 Dogfish Muscle, SRM 612 Trace Elements in Glass and SRM 2976 Mussel Tissue. All measurements were completed in triplicate, and sample cups were removed from the instrument and repositioned between each measurement. Concerning the ICP-OES comparison, SRM 2976 Mussel Tissue and ERA Metals in Soil D069-540 (Golden, CO) were used to evaluate the recoveries for the method.

2.2. *Archived laboratory samples*

A broad selection of archived samples that had been collected previously for various public health investigations were used for evaluation purposes in this study. Many of the HMPs (n = 22) and CP (n = 12) were provided by the New York City Department of Health and Mental Hygiene's (NYC DOHMH) Division of Environmental Health, and had been the subject of investigations by that agency. Most of the samples had been confiscated during retail inspections and/or as a result of product recalls conducted by NYC DOHMH (Dr Paromita Hore, NYC DOHMH, personal communication). Nearly all of the products had been imported, and several had been associated with childhood lead poisoning cases in New York City. Foodstuff, including imported spices and tea samples (ES, n = 4), were also analysed. Archived samples had been stored at room temperature in their original packaging.

2.3. *XOS prototype environmental analyser*

An optimised prototype instrument was assembled by X-Ray Optical Systems, Inc., (XOS, East Greenbush, NY) specifically for use in this study (Figure 1a). The prototype analyser was developed from earlier iterations that demonstrated the feasibility of the approach. The prototype analyser is equipped with a 50-W molybdenum (Mo) anode X-Ray tube as the excitation source, a shutter, and three multi-segment DCC optics, designed to generate monochromatic excitation energies at 7, 17.5, and 31 keV during a pre-programmed measurement sequence. The diameter of the beam spot at the measurement site is ~1 mm. A silicon drift detector (SDD; Vortex-90EX, SII Nano Technology, Northridge, CA) is utilised for energy dispersive detection of fluorescent X-Rays. The XOS prototype instrument bench top unit evaluated in this study weighs ~20 kg and measures 38 (W) × 45 (D) × 45 (H) cm (Figure 1b).

For field use, the instrument is transported using a collapsible cart. It is equipped with a safety interlock and is fully shielded. Nonetheless, staff wore personal dosimeters to monitor their exposure to ionising radiation during all XRF operations. Instrument operation and data reporting are controlled with an integrated touch screen; a separate monitor was used for laboratory-based studies. Quantitation is accomplished *via* XOS' proprietary software based on fundamental parameters (FPs), which reports results for more than 30 elements in parts-per-million (ppm) units, i.e. mg/kg or mg/L. User selectable parameters include substrate (metal, non-metal, or liquid) and excitation type (tri-chromatic through a combination of three separate optics and a 50-W Mo source). Although the prototype instrument was equipped with a tri-chromatic DCC
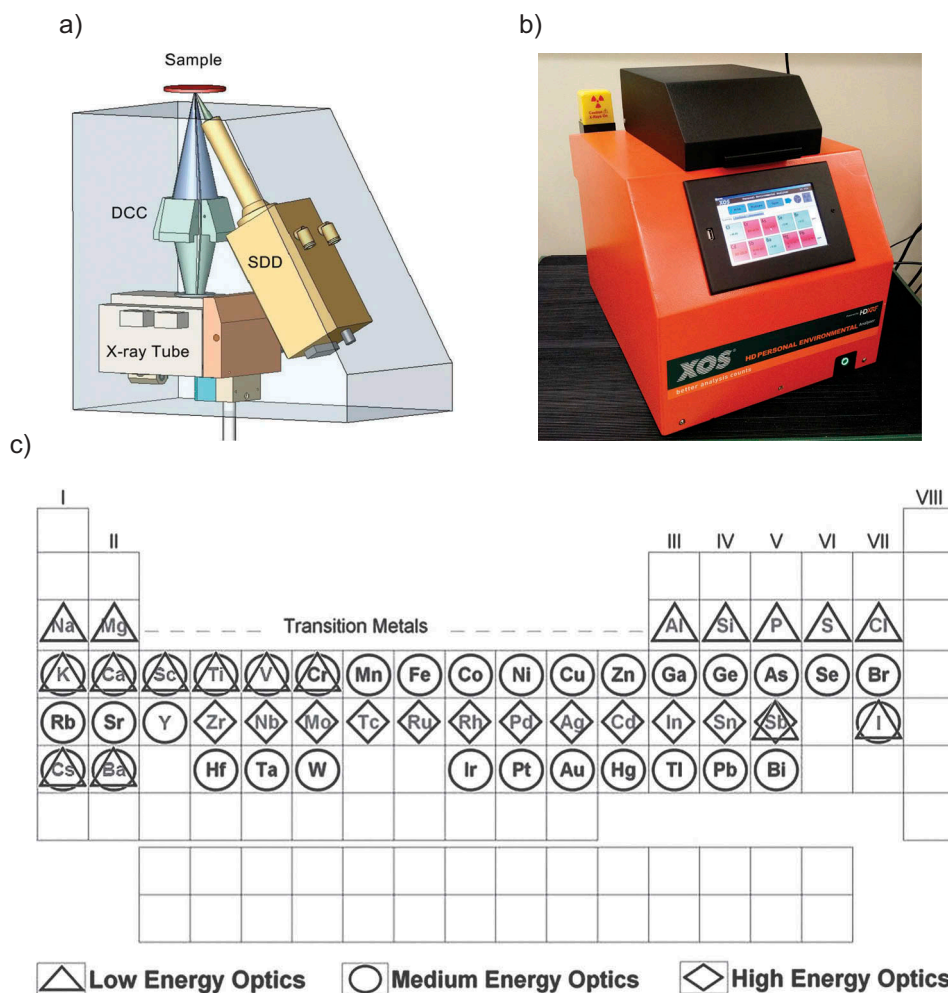
Figure 1. (a) Optical configuration of the XOS prototype analyser. (b) Image of the XOS prototype instrument – computer monitor is also attached to the instrument. (c) Elements measurable by the respective optics of the instrument.

excitation optic, only the 17.5 and 31 keV excitation energies were utilised for this study (the 7 keV beam was not necessary for this application). Figure 1c shows those elements that can be fluoresced by each of the three optics. For public health purposes and this study, only the medium- and high-energy optics were needed to capture the major toxic elements of interest: Pb, Cd, Hg, and As. Each sample measurement was made using the 'non-metal' substrate mode. The analyser was operated with a 3.5-minute count time, which was fixed by the manufacturer for this particular prototype instrument.

A standard 32-mm diameter × 24 mm height XRF sample cup (Premier Lab Supply, Port St. Lucie, FL) was used with a 4-µm thick Ultralene window (Chemplex Industries, Palm City, FL). The polyethylene cup was filled to approximately ½ full, typically 2–6 grams of sample, equivalent to ~1 cm, which ensured infinite path thickness. The XRF

cups were sealed with end-caps, and prepared samples were utilised repeatedly throughout the study. Aqueous standards were prepared by diluting 10,000 µg/mL (Inorganic Ventures, Christiansburg, VA) or 1000 µg/mL (Spex Certiprep, Metuchen, NJ) single element standards with 18.2 MΩ.cm double-deionised water produced with a Barnstead Nanopure system (Thermo Scientific, Waltham, MA). Each aqueous standard (5 mL) was placed in an uncapped cup, which was discarded daily at the completion of analysis.

Archived samples were typically pills or tablets that were ground to a coarse powder able to pass through a 2-mm (USS#10) sieve. Powders were prepared simply by using a pestle to crush whole tablets placed inside a Whirl-Pak (Nasco, Fort Atkinson, WI), and secured within a piece of folded card stock. This simplified sample preparation approach was selected due to its feasibility for field use where cleaning a common mortar would be impractical and would likely lead to cross-contamination. Preparation for XRF analysis entailed placing about 2.75–5.75 g of coarse powdered sample into the aforementioned 32-mm polyethylene XRF sample cup with a 4-µm Ultralene window. Once prepared, the open end of the sample cup was sealed and the sample was used for all subsequent XRF measurements on both the XOS prototype and Niton instruments. In some cases, samples (n = 5) consisted of pastes or creams, and were analysed by placing the product directly into a sample cup (~2 cm thickness). All sample preparation was carried out in the Wadsworth Center's Trace Elements Laboratory using protocols (gloves, disposable plastic ware, etc.) designed to avoid contaminating either the samples or the laboratory. Regardless, all samples were measured in triplicate on both the XOS prototype and the Niton, with the sample repositioned between each measurement. A silicon dioxide (SiO_2, 99.999%) blank (provided by the instrument manufacturer) was measured each day of the analysis.

2.4. *Niton XL3t GOLDD XRF analyser*

A commercial handheld XRF instrument, the Niton (Thermo Scientific, Tewksbury, MA), was also evaluated in this study, since it is intended for a wide variety of applications, including toy testing and alloy identification. The Niton is equipped with a 2-W Au anode tube source, and primary filters that produce excitation beams of different energies, with a spot size of 8 mm. It also uses an SDD to detect fluorescent X-Rays that are analysed using Thermo's proprietary software to yield quantitative results based on mass fraction, i.e. mg/kg or parts-per-million (ppm). The Niton measurements in this study were conducted using the soil substrate mode with the analyser mounted in a SmartStand (Thermo Scientific, Tewksbury, MA) that allows for remote control *via* a PC, and more closely mimics a bench top instrument. The SmartStand ensures that the Niton device is firmly secured, and provides for improved measurement repeatability by reducing variability, that results from variable positioning of the analyser when used in the manual handheld mode. In addition, use of the SmartStand reduces unnecessary exposure to scattered X-Rays. As with the XOS prototype instrument, staff wore personal dosimeters to monitor their exposure to ionising radiation during all operations with the Niton analyser. The same samples prepared for analysis on the XOS prototype instrument were reanalysed on the Niton. A two-minute measurement time was selected for

use with the Niton instrument, based on guidance provided by the manufacturer. While longer count times would decrease measurement uncertainty, this must be balanced against a decrease in sample throughput.

2.5. *ICP-OES instrumental analysis*

For comparison purposes, samples analysed by XRF (non-destructive) for the evaluation study were also analysed by ICP-OES (US EPA Method 6010C) following acid digestion (destructive). Digested samples were analysed for 17 elements using a PerkinElmer Optima 5300DV ICP-OES instrument (PerkinElmer Inc., Shelton, CT 06484). The plasma source was viewed axially for all elements (except Sr, which was viewed radially). A concentric nebuliser and cyclonic spray chamber were used to transfer samples into the plasma source. The Optima is equipped with an echelle polychromator with a solid-state segmented-array, charge-coupled-device detector. The optical system was purged with Ar gas during operation to improve sensitivity for elements with wavelengths below 190 nm, and the alignment optimised with 1 mg/L Mn solution. The analytical procedure followed EPA Method 6010C, including calibration, initial, and continuous calibration verification. Calibration and spike standards were obtained from High-Purity Standards (Charleston, SC 29432); the calibration verification standards were obtained from AccuStandard (New Haven, CT 06513). Table 1 lists the elements determined, along with the analytical wavelength selected, plasma-viewing position, and other instrumental parameters. ICP-OES performance data, based on analytical recoveries for ERA Metals in Soil D069-540 ($n = 7$), are also given in Table 1.

Prior to ICP-OES analysis, all samples were acid digested using a procedure based on EPA Method 3050B. Approximately 50 mg of tablet (or powder) was weighed into a

Table 1. ICP-OES[†] parameters, recovery data, and method detection limits.

Element	Wavelength (nm)	Plasma-viewing position	Certified value (mg/kg)	ICP-OES* (mg/kg)	Recovery (%)	MDL[§] (mg/kg)
As	188.979	Axial	109	107	98	2.3
Ba	233.527	Axial	325	300	92	0.2
Cd	214.44	Axial	110	88	80	4.9
Cr	267.716	Axial	93.4	80	86	0.3
Co	228.616	Axial	133	113	85	0.03
Cu	324.752	Axial	74.7	68	91	0.5
Fe	259.939	Axial	13100	11600	89	11
Pb	220.353	Axial	152	128	84	11
Mn	257.61	Axial	443	375	85	0.1
Hg	194.227	Axial	16.3	13	80	1.0
Ni	231.604	Axial	109	90	82	0.3
Se	196.026	Axial	207	18	87	0.8
Sr	421.552	Radial	111	98	88	0.1
Sn	189.927	Axial	135	130	96	3.1
Ti	334.94	Axial	193	215	111	0.2
V	292.402	Axial	110	100	91	0.1
Zn	213.857	Axial	299	260	87	8.4

[†] PE Optima 5300DV operated with: 1500 W RF power, 0.55 L/min nebuliser flow rate, 0.2 L/min auxiliary flow rate, and 15 L/min plasma flow rate; signal integration times ranged from 5 s to 20 s; read delay time 55 s; rinse time 55 s ($n = 3$ replicates).
*Recovery data are based on the analysis of ERA Metals in soil D069-540 ($n = 7$).
[§]MDL calculated based on ISO/IUPAC guidelines: 3 SD of blank ($n = 10$); mg/kg value determined for 50 mL sample volume and 50 mg sample mass.

disposable borosilicate glass test tube (Kimble Chase, Vineland, NJ), and 100 µL of a 500 µg/mL Au solution, prepared from a 10,000 µg/mL standard (Inorganic Ventures, Christiansburg, VA), was added to the tube, along with 5 mL of 50% (v/v) trace metal grade HNO_3 (Fisher Scientific, Pittsburgh, PA). Addition of 1 mg/L Au as $AuCl_3$ is effective at preventing Hg volatilisation by maintaining Hg^{2+} ions in solution [23]. Four heating and reflux steps of approximately 30 minutes each were completed at 90°C using a hot block. After an initial heating, 3 mL of concentrated HNO_3, 2 mL of 18.2 MΩ.cm deionised water, 3 mL of 30% (v/v) H_2O_2 (J.T. Baker, Phillipsburg, NJ), and 3 mL of concentrated trace metal grade HCl (Fisher Scientific, Pittsburgh, PA) were added prior to successive heating steps. The samples were cooled before each addition and before filtration with a 1-µm Teflon filter (SCP Science, Champlain, NY). The samples were brought to final 50 mL volume with 18.2 MΩ.cm deionised water and stored in a polypropylene tube (SCP Science, Champlain, NY) pending multi-element analysis by ICP-OES.

Samples were separated into two batches for analysis by ICP-OES based on expected Hg content as determined by XRF. Samples with low-Hg content were analysed before those with very elevated Hg to minimise potential carryover. Diluent and rinse were prepared with 18.2 MΩ.cm deionised water and 5% (v/v) HNO_3, 2% (v/v) HCl, and 1 mg/L Au. In many cases, it was found necessary to analyse both undiluted and diluted samples to ensure that a wide range of analytes were determined within the calibration region established for ICP-OES. Standards analysed in addition to the typical 5-point calibration curve indicated the linear dynamic range (LDR) reached 50 mg/L for most of the elements of interest, which reduced the overall number of dilutions required significantly. ERA Metals in Soil D069-540, a quality control (QC) material containing the 17 analytes of interest, was analysed in each run along with an aqueous digestion spike, digestion blank, diluent blank, and sample duplicate, consistent with standard EPA approved methods of analysis. The accuracy of the ICP-OES procedure was validated against NIST SRM 2976 Mussel Tissue (data not shown).

3. Results and discussion

3.1. *XRF instrumental performance*

Instrumental sensitivity and the LDR for the XOS prototype were determined for Pb, As, Hg, and Cd using single-element aqueous standard solutions up to 10,000 µg/mL. The data are presented as aqueous calibration curves in Figure 2.

Sensitivity was higher for As, followed by Pb and Hg, while Cd had poorer sensitivity. With the exception of Cd, which was linear up to 10,000 µg/mL ($R^2 = 0.98$), the responses for As, Pb, and Hg are only linear up to ~1000 µg/mL. The deviation from linearity is likely due to self-absorption of the fluorescence emitted by the sample at the higher concentrations, although there may be other factors too. The poorer precision observed at some elevated concentrations was unexpected and cannot be explained adequately. Despite the lack of linearity for As above 1000 µg/mL, the predicted values for the aqueous standards as reported in µg/mL by the FP-software showed a negative bias of −22% and −8% for the 5000 µg/mL and 10,000 µg/mL standards, respectively. It would appear that the FP-software is correcting for non-linearity, to some extent.
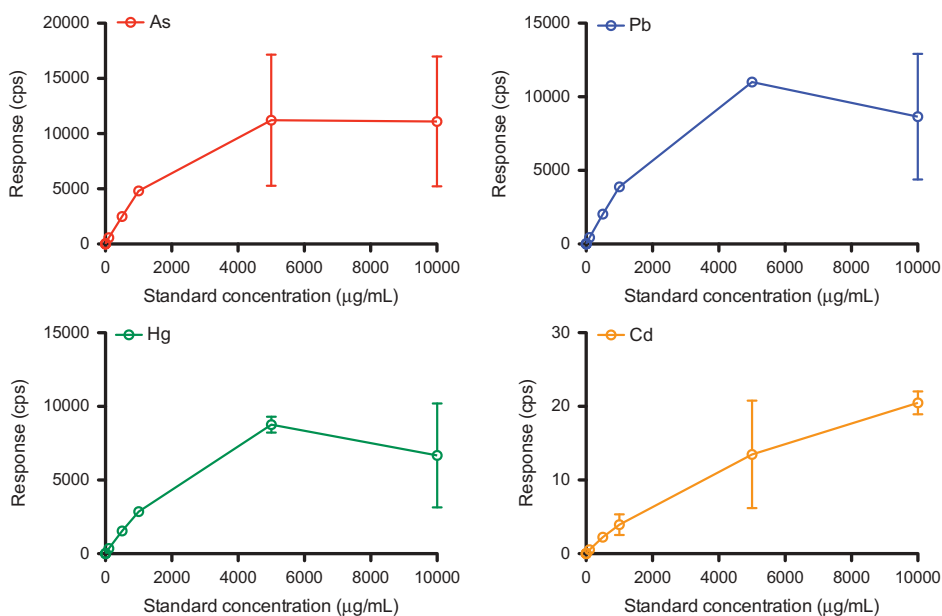
Figure 2. Sensitivity and linearity for As, Cd, Hg, and Pb by XOS prototype instrument.

Table 2. Instrumental and detection limits for the XOS prototype analyser and the Niton based on the analysis of an archived soil sample.

Element	XOS prototype XRF		Niton	
	IDL (mg/kg)	MDL[§] (mg/kg)	IDL (mg/kg)	MDL[¶] (mg/kg)
As	0.1	2	2.5	7
Cd	1.2	36	6.6	14
Hg	0.1	1	4.0	2
Pb	0.1	2	3.4	7
Ba	4.9	40	28	65
Co	0.2	6	18	4
Cr	0.8	7	14	14
Cu	0.1	17	10	22
Fe	0.2	45	23	64
Mn	0.4	37	37	85
Ni	0.2	2	35	5
Se	0.1	14	2.0	6
Sn	0.2	28	19	12
Sr	0.1	2	<1	3
Ti	2.3	54	25	12
V	1.4	9	17	13
Zn	0.1	34	5.1	23

[§] $n = 9$ days (triplicate within day).
[¶] $n = 5$ days (triplicate within day).
IDL is instrument detection limit and is defined within the instrument software as '≤' and is based on the analysis of a SiO_2 blank.
MDL is method detection limit based on analysis of an archived soil sample. See text for details.

Instrumental detection limits (IDLs) for the two XRF devices are shown in Table 2. The IDL is based on the analysis of a SiO_2 blank, and is analogous to what is typically reported in other areas of analytical atomic spectrometry, where aqueous solutions are used to obtain IDL data [24]. The IDL for this study was obtained from the XRF

instrument software, where values are reported as either 'not detected (ND)', '<limit of detection (LOD)', or '<'. According to IUPAC, the IDL may not accurately reflect performance with more complex samples, e.g. vegetation, food, soil, pharmaceuticals, etc., and they recommend a practical approach to detection limits that includes the sample matrix. A more rigorous approach is to estimate the 'method' detection limit (MDL) by analysing a complex matrix containing multiple detectable elements, and calculating the MDL using the following equation [25]:

$$MDL = \frac{3\sqrt{B}}{P}C, \qquad (1)$$

where C is the concentration of the element, and B and P are the count rates for the background and characteristic peak, respectively. MDL values are an indication of analytical performance, but they are matrix specific.

For this study, repeated analyses of an archived soil sample were carried out over nine days on the XOS prototype and over five days on the Niton, to estimate the MDL for 17 elements (Table 2).

The archived soil sample provided a convenient matrix for the MDL study and contained endogenous elements at levels that were within one order of magnitude of the MDL for 11 of the 17 elements studied, while five were within two orders of magnitude. The sole exception was Fe, which is a major component of most soils. A comparison between the IDL and MDL data (based on a soil matrix for the latter) shows that, for the Niton, the agreement is within a factor of 4–5, whereas for the XOS prototype instrument, the IDL is more typically an order of magnitude lower than the corresponding MDL. With respect to the Niton, the observed discrepancies between some poorer IDL values, compared to better MDL estimates for some elements (e.g. Ni, Ti, and Co), is probably due to the different algorithms used to calculate these parameters. The lower MDL values for the XOS prototype instrument, when compared to the Niton, are most likely due to a combination of factors, including the use of the DCC monochromatic optic, which increases the signal-to-noise ratio, a higher power source and longer measurement time (3.5 versus 2 min), which collectively yield increased sensitivity for many elements. In several cases (Se, Ti, Sn, and Cd), the MDL performance of the Niton analyser is slightly better than for the XOS prototype. The reason for this may be related to poorer precision (noise) as the smaller beam size of the XOS prototype may be interrogating a non-homogeneous soil surface, while the Niton beam averages the signal over a larger sample area.

Accuracy and precision of the XOS prototype instrument were evaluated using three CRMs including Mussel Tissue, Tuna Fish, and Dogfish Muscle. NIST SRM 612 Trace Elements in Glass was also analysed for informational purposes. Most of the CRMs were analysed on a single day with the instrument operated in the non-metal substrate mode. Between-day analytical performance was assessed by analysing SRM 2976 Mussel Tissue over five days (Table 3)

For the within-day data, performance was deemed acceptable for field-screening purposes if the absolute bias was <25% for certified values in the range of 100–1000 mg/kg, and <50% for certified values <100 mg/kg. Low levels (<5 mg/kg) of As and Hg were also measured in biological CRMs with a bias of +4% and −40%, respectively. Results for these CRMs may be considered indicative of what is possible

Table 3. Accuracy, precision and uncertainty of the XOS prototype instrument based on analysis of certified reference materials.

CRM	Matrix	Element	Certified (mg/kg)	±U	XOS prototype (mg/kg)	%RSD	%Bias	n	Variability
BCR 627	Tuna Fish Tissue	As	4.8	0.3	5	0	4	5	Within-day
DORM 2	Dogfish Muscle	As	18	1.1	17	9	−7	10	Within-day
		Cr	34.7	5.5	23	29	−33		
		Cu	2.34	0.16	2	0	−15		
		Fe	142	10	102	19	−28		
		Mn	3.66	0.34	ND	–	–		
		Hg	4.64	0.26	3	15	−40		
		Ni	19.4	3.1	11	22	−44		
		Se	1.4	0.09	2	23	29		
		Zn	25.6	2.3	25	28	−2		
SRM 612	Glass Matrix	Ba*	41		75.5	30	84	5	Within-day
		Co*	35.5	1.2	43.6	5	23		
		Cu*	37.7	0.09	51	5	35		
		Au*	5		ND	–	–		
		Fe	51	2	36.4	8	−29		
		Mn*	39.6	0.8	24.4	8	−38		
		Ni	38.8	0.2	50.6	6	30		
		Ag	22	0.3	18.2	18	−17		
		Sr	78.4	0.2	62.4	2	−20		
		Ti*	50.1	0.8	ND	–	–		
		Pb	38.57	0.2	35.4	3	−8		
		K*	64		267	71	317		
		Rb	31.4	0.4	29.4	3	−6		
SRM 2976	Mussel Tissue	As	13.3	1.8	13	4	−4	5	Between-day
		Pb	1.19	0.18	2	39	77		
		Br*	329		289	3	−12		
		Ca*	7600		6055	9	−20		
		Cl*	57000		52184	5	−8		
		Fe	171	4.9	157	9	−8		
		K*	9700		7610	7	−22		
		Mn*	33		28	10	−16		
		P*	8300		7974	9	−4		
		Rb*	4.14		5	16	10		
		S*	19000		14332	2	−25		
		Se	1.8	0.15	1	59	−31		
		Sr*	93		66	3	−29		
		Zn	137	13	137	6	<1		

* reference or informational value; ±U is the expanded uncertainty from the CRM certificate of analysis; PE = polyethylene.

for 'real world' samples such as Ayurvedic medicines or herbal supplements. Within-day precision was typically better than 10% for analytes meeting the acceptance criteria, except for NRC DORM-2 Dogfish Muscle, where the %RSD was inflated due to measured values approaching the IDL. For the between-day measurements, variability was <20% RSD except for Pb and Se, for which the certified mass fractions were <2 mg/kg. For the reference material SRM 2976 Mussel Tissue, a downward drift in measured As values was apparent between days 6 and 9, while a positive drift occurred for Pb over the same period. This is probably due to sub-optimal deconvolution by the FP software of the As K_α and Pb L_α characteristic lines that appear around 10.5 keV. For comparison in the same sample, within-day variability ($n = 3$) was <8% relative for As and <50% relative for Pb (data not shown).

It is noted that, in general, the % bias increases at lower concentrations, such as for Pb at 1.19 mg/kg in SRM 2976, and that a high bias is not surprising for low Z elements

such as *K* at a concentration of 64 mg/kg in SRM 612., Additionally, high *Z* elements that have low *L* energy lines also show a high bias, such as Ba at a concentration of 41 mg/kg in SRM 612. Overall, the sensitivity of the XOS instrument for a given element depends on the difference between the DCC optic (thence energy) that is used and the excitation energy of the element. In general, the smaller the difference, the better the excitation efficiency, and thus, the sensitivity.

3.2. *ICP-OES method performance*

The ICP-OES comparison method (EPA Method 6010C) used for the determination of metals in soil was validated at the Wadsworth Center as part of the laboratory's requirements for accreditation under the American Association for Laboratory Accreditation (A2LA) as a PT provider for environmental testing laboratories [26]. Analytical recoveries based on repeated analysis of an archived QC soil sample containing the 17 elements of particular interest for this study were found to be within ±20% (Table 1). MDL determined according to the IUPAC/ISO Harmonized guidelines (3SD of 10 digestion blank measurements) are also shown in Table 1. Duplicate analyses of SRM 2976 Mussel Tissue for Cd, Cu, Se, and Zn were within 87–102% of the assigned value, while values for Sr and As were low (71–75%). Additional aqueous pre-digestion spikes were conducted and recoveries were within ±10% of the expected value (data not shown). Four samples (Emperor's Tea Pill, Mahayogaraj Guggulu, Litargirio, unlabelled powder) were digested and analysed in duplicate, and the difference in duplicates was <15%.

3.3. *Comparison of archived sample data by XRF with ICP-OES*

A total of 38 archived samples, including medicinal products, cosmetics and foods, were analysed for As, Ba, Cd, Cr, Co, Cu, Fe, Hg, Ni, Mn, Pb, Se, Sr, Sn, Ti, V, and Zn on the XOS prototype, on the Niton, and results compared to data obtained by ICP-OES. Samples analysed were categorised as either HMP, ES, or CP. Table 4 shows the results for five representative HMPs originating from the Indian subcontinent, and one from China.

The complete dataset for all 22 HMPs analysed by each of the three analytical methods for all 17 elements (*n* = 1122 results) can be accessed as an electronic supplementary information (ESI) files. All HMP samples were analysed in triplicate using both XRF devices. A portion of the same original sample was acid digested and analysed for multiple elements by routine ICP-OES, for comparison purposes. For each detectable value obtained by XRF, the SD (*n* = 3) is shown in parentheses.

Table 5 shows representative results obtained for four CPs and one ES that originated from the Indian subcontinent.

Again, a complete dataset with results for all 12 CPs and 4 ES samples, by each XRF device, and comparison data from ICP-OES, for all 17 elements (*n* = 816 results) are available as ESI files. Each of the HMP, CP, and ES samples was analysed in singlet by ICP-OES; however, the uncertainty in the ICP-OES value is estimated at approximately ±20% based on the QC (Table 3). Missing values in Tables 4 and 5, and in their associated ESI files, were either below the MDL (ICP-OES) or the XRF instrument software (XOS and/or Niton) did not report it. In some cases, the minimum reporting limits (i.e. the IDL) for the

Table 4. Results obtained by ICP-OES (n = 1), and XRF (n = 3, mean (SD)) for a representative number of HMPs samples; blank results indicate result <MDL by ICP-OES or <IDL by XRF methods. Units are mg/kg, except where indicated.

Name, manufacturer	Lakshmivilash Ras, Shree Baidyanath Ayurved Bhawan Pvt. Ltd.			Mahayogaraj Guggulu, Shree Baidyanath Ayurved Bhawan Pvt. Ltd.			Suketu, Sohum Bioenergetis Natura Health Care		
Origin	India			India			India		
Indication	Chronic fever & cough			Rheumatic pain					
Method	ICP-OES	XOS prototype	Niton	ICP-OES	XOS prototype	Niton	ICP-OES	XOS prototype	Niton
As	28	65 (4)	46 (15)	0.73%	0.40 (0.01)%	1.3 (0.06)%	720	2930 (463)	736 (625)
Cd					17 (3)	178 (4)			
Hg	5.5%	8.9 (0.40)%	4.6 (0.06)%	4.7%	3.0 (0.09)%	2.9 (0.14)%	6.0%	17 (1.3)%	2.9 (2.5)%
Pb		20 (12)		4.5%	4.9 (0.10)%	6.8 (0.09)%		125 (136)	
Ba	300			132	160 (<1)	530 (40)	12		
Co	9.2		163 (<1)	6			0.6	18 (12)	
Cr	38	7 (7)		15	105 (16)	43 (<1)	16	60 (18)	
Cu	19			173	151 (7)	365 (25)	32		
Fe	0.96%	2.3 (0.4)%	1.9 (0.03)%	2.9%	6.7 (0.2)%	13 (0.62)%	0.13%	0.81 (0.01)%	0.27 (0.21)%
Mn	86	222 (40)	179 (45)	526	749 (2)	1785 (224)	34	189 (34)	
Ni	43	54 (11)		23	16 (12)	573 (79)	7.9		45 (<1)
Se						45 (<1)			
Sn	6.7	19 (2)		1.1%	1.8 (0.07)%	3.8 (0.003)%	56	76 (56)	
Sr	81			62	71 (6)		23	251 (212)	
Ti	406	1456 (288)	852 (30)	303	877 (156)	841 (97)	36	174 (97)	130 (89)
V	7.7	22 (15)		21	91 (16)	68 (<1)	2.2		
Zn	45	488 (55)	304 (24)	330	149 (40)	880 (11)	17	1019 (<1)	189 (144)

Name, manufacturer	Garbhapal Ras			Emperor's Tea Pill, Kingsway Trading Inc.			Kumar Kalyan Ras Unknown		
Origin	India			China					
Indication	Healthy pregnancy			Natural balance					
Method	ICP-OES	XOS prototype	Niton	ICP-OES	XOS prototype	Niton	ICP-OES	XOS prototype	Niton
As	0.05%	0.15 (0.09)%	0.72 (0.07)%	25	17 (3)	234 (19)	422	289 (160)	987 (359)
Cd		30 (<1)	122 (9)					32 (33)	
Hg	5.1%	2.8 (0.60)%	2.9 (0.18)%	0.71%	0.39 (0.02)%	0.40 (0.008)%	15%	6.2 (0.70)%	6.8 (2.5)%
Pb	3.3%	3.3 (0.98)%	4.9 (0.45)%	0.49%	0.22 (0.02)%	0.44 (0.005)%	0.34%	0.17 (0.04)%	0.27 (0.11)%
Ba	11.4		147 (19)	1506	1108 (189)		177		149 (<1)
Co	0.7			0.7			14	17 (<1)	
Cr	2.7	213 (15)		4.6			133	246 (173)	120 (58)
Cu	39	21 (20)	76 (8)	27	9 (0.6)	35 (5)	310	100 (39)	870 (523)
Fe	0.98%	2.1 (0.6)%	3.8 (0.3)%	593	777 (22)	1200 (14)	14%	9.6 (1.4)%	44 (17)%

(*Continued*)

Table 4. (Continued).

Name, manufacturer	Garbhapal Ras			Emperor's Tea Pill, Kingsway Trading Inc.			Kumar Kalyan Ras Unknown		
Origin	India			China					
Indication	Healthy pregnancy			Natural balance					
Method	ICP-OES	XOS prototype	Niton	ICP-OES	XOS prototype	Niton	ICP-OES	XOS prototype	Niton
Mn	110	93 (53)	234 (78)	28	37 (2)		0.11%	0.09 (0.05)%	0.38 (0.16)%
Ni	2.7		296 (120)	1.9	0.4 (0.1)		67	18 (12)	391 (46)
Se			57 (8)	4.2	2 (<1)	15 (2)		109 (6)	
Sn	0.70%	1.2 (0.5)%	1.9 (0.16)%	3.5	4 (0.7)		301	0.26 (0.22)%	0.08 (0.06)%
Sr	94	78 (2)		27	18 (4)	25 (0.6)	78	0.10 (0.02)%	
Ti	27	194 (167)	235 (78)	10	385 (102)	171 (<1)	0.09%	0.14 (0.11)%	0.13 (0.04)%
V	1.2			0.6	188 (51)		7.6	76 (23)	
Zn	82	104 (53)	317 (67)	0.19%	0.13 (0.02)%	0.32 (0.01)%	496	248 (389)	1671 (681)

Table 5. Results obtained by ICP-OES ($n = 1$) and XRF ($n = 3$, mean (SD)) for a representative number of CPs and ES samples; blank results indicate result <MDL by ICP-OES or <IDL by XRF methods. Units are mg/kg, except where indicated.

Type	CP			CP			CP		
Name, manufacturer	Personal Kajal, Blue Heaven Cosmetics Ltd.			Kohl Aswad, Hashmi			Surmi Special, Hasmi		
Origin	India			Pakistan			Pakistan		
Method	ICP-OES	XOS prototype	Niton	ICP-OES	XOS prototype	Niton	ICP-OES	XOS prototype	Niton
As					0.04 (0.04)%	8.7 (0.34)%	7.2	359 (34)	8.2 (0.11)%
Cd		10 (13)		13	1.1 (0.9)	1.1 (0.17)%	16	0.4 (0.2)	2.6 (2.4)%
Hg				3.7			2.5		
Pb	25	3 (2)		20%	4.9 (2.9)%	>100 (2.3)%	19%	3.0 (0.09)%	>100 (0.61)%
Ba	2.5			60	192 (<1)	5.1 (0.84)%	96	21 (<1)	12 (11)%
Co	2.6	38 (<1)		0.3	3 (<1)		2.2		
Cr	3.9	14 (15)		0.4	18 (<1)		1.1		
Cu	3.3	3 (<1)	6.6 (0.76)%	348	41 (20)		0.16%	0.02 (0.002)%	0.6 (0.04)%
Fe	2.8%	1.0 (0.9)%	319 (56)	213	112 (22)	713 (116)	720	108 (9)	
Mn	190	84 (99)		1.4	15 (<1)		15.4		
Ni	4.0	5 (6)		0.8	81 (<1)		1.8		
Se	0.8	0.2 (0.1)		0.9					
Sn		34 (58)			3 (2)	2.7 (0.48)%		1 (<1)	6.3 (5.7)%
Sr	62	185 (301)		109	246 (<1)			6 (<1)	
Ti		65 (83)		0.4	69 (<1)				
V				0.3	67 (<1)	44 (1)			
Zn	6 (<1)	6 (<1)		0.54%	0.08 (0.01)%	2.2 (0.04)%	0.55%	0.07 (0.004)%	2.5 (0.02)%

Type	CP			ES		
Name, manufacturer	Kajal powder			Chili powder		
Origin	Unknown			India		
Method	ICP-OES	XOS prototype	Niton	ICP-OES	XOS prototype	Niton
As	37	263 (176)	8.7 (0.40)%		6 (2)	14 (6)
Cd		0.6 (0.3)	1.7 (1.2)%		1 (<1)	
Hg	3.2					
Pb	20%	3.7 (0.60)%	>100 (4.5)%	193	218 (11)	261 (19)
Ba	162		7.9 (5.7)%	32	34 (12)	
Co	0.5			0.8	2 (<1)	
Cr	0.5	4 (5)		47	54 (10)	84 (8)
Cu	152	7 (1)		11	12 (0.6)	17 (1)
Fe	605	68 (6)	897 (<1)	228	295 (38)	273 (51)

(*Continued*)

Table 5. (Continued).

Type	CP			ES		
Name, manufacturer	Kajal powder			Chili powder		
Origin	Unknown			India		
Method	ICP-OES	XOS prototype	Niton	ICP-OES	XOS prototype	Niton
Mn	7.3		0.16 (0.04)%	19	24 (3)	
Ni	1.1			2	3 (<1)	
Se		8 (2)			0.3 (0.1)	
Sn		0.9 (0.2)	4.0 (2.8)%		20 (0.6)	
Sr	193			13	13 (<1)	17 (0.5)
Ti	0.6	98 (48)		3.9	34 (10)	55 (10)
V	0.4	16 (19)		0.1	7 (1)	
Zn	0.30%	385 (189)	1.5 (0.18)%	19	23 (2)	23 (3)

XRF software were lower than the MDL calculated according to the ISO/IUPAC guideline. Descriptive information available on each of 38 samples sample analysed, including the manufacturer, country of origin, indication, and labelling details, is also given in Tables 4 and 5, and in the ESI files.

The elements Zn and Ti were detected by both XRF instruments in nearly all of the samples analysed. Values for As, Cu, Hg, and Pb were also reported in many of the samples. However, based on the comparison with ICP-OES, several false positive results were evident for As when Pb was also present. This is a well-known problem in energy dispersive XRF due to overlap of the As Kα and Pb Lα lines at 10.53 keV and 10.55 keV, respectively. Both XRF instruments calculate results for As and Pb using FP-software that is designed to deconvolute the spectrum, and correct for the overlap. However, it is clear from the data reported here that the overlap correction is not always successful, and caution is warranted when As and Pb are both present. Another possibility for spectral overlap can occur from high levels of Fe, i.e. Fe sum peaks can cause a false positive for Pb in the presence of As. For Co, Ni, and Se, ICP-OES found values were very often near or below the XRF minimum reporting limits for both the XOS prototype and Niton instrument. Consequently, several false positive results for Co, Ni, and Se were evident by XRF.

In one case, the Lakshmivilash product from India (Table 4) was found to contain 300 mg/kg Ba via ICP-OES. Yet both the XOS prototype and Niton analyser reported less than the manufacturer's detection limit. The most likely explanation for this false negative discrepancy is not that these instruments are unable to detect Ba at 300 ppm, but rather the software cannot accurately fit the X-Ray peak above the background for this particular sample. In some cases, the background may be so high that it completely obscures the peak, thereby resulting in a false negative. It is possible that use of the low energy optic in the XOS prototype instrument might have addressed this.

Discrepancies between XRF-reported data and ICP-OES data can be investigated in more detail using difference plots, i.e. where the difference between the XRF and ICP-OES results are plotted as a function of increase in the latter. Figure 3 shows difference plots for the elements Pb, As, and Hg obtained using the XOS prototype and the Niton analyser with HMP, ES, and CP samples. The elements were selected based on their public health significance. The dashed lines in Figure 3 denote an arbitrary performance criterion of ±50% relative to ICP-OES, and might be considered acceptable for screening purposes when attempting to identify gross contamination.

However, a negative 50% bias at lower levels could result in materials being erroneously identified as 'safe' when they are contaminated, i.e. a false negative. The nature of a difference plot requires that there be two detectable results from both techniques. Thus, only detectable (ICP-OES >MDL) or reportable data (XRF) can be included in these plots. Given that the levels of Pb, As, and Cd found in these samples cover several orders of magnitude, the difference plots shown in Figure 3 are arranged such that the left-hand panels (a–c) represent the full range of contents found (up to wt.% levels), while the right-hand panels (d–f) show the lower range of values detected.

It is evident that a large number of data points in Figure 3 fall outside the ±50% dashed lines. Overall, the Niton tends to have a positive bias, while the XOS prototype instrument has a negative bias, though performance appears to be element and matrix specific. Performance for Pb on both the XOS and Niton was generally within ±50%
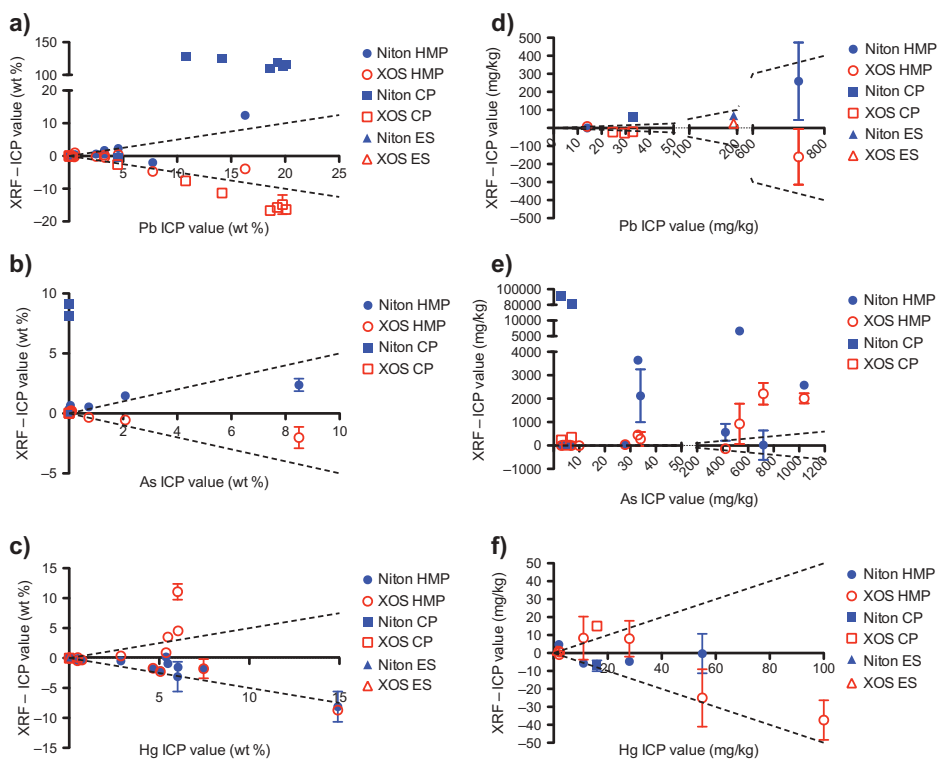
Figure 3. Difference plots (XRF – ICP-OES value) for Pb, As, and Hg in powdered samples measured with the XOS prototype and the Niton; left side shows all results, right side includes only low mg/kg range; XRF(n = 3, error bars ± SD); the dashed lines indicate ±50% of reference value; HMP –herbal medicine product; ES –ethnic spice; CP – cosmetic product.

(relative to ICP-OES) up to 800 mg/kg, while above 10% by weight, it was much poorer, with the Niton being positively biased and the XOS prototype instrument negatively biased. Most of the samples showing poor agreement were CP such as *kohl*, *surma*, or *kajal*, which are fine black powders often consisting of lead sulphide that is applied to the conjunctive surface of the eyelids. However, both the XOS and Niton instruments correctly identified gross Pb contamination in the CP samples.

A sample of chili powder imported from India that contained approximately 190 mg/kg Pb based on analysis by ICP-OES was reported as approximately 220 mg/kg Pb using the XOS prototype analyser (16% bias) and approximately 260 mg/kg on the Niton (37% bias).

A second example is the Mahayogaraj Guggulu pill, an HMP manufactured in India and labelled for use with rheumatic pain. The sample was found to contain 4.5 wt.% Pb, 4.7 wt.% Hg, and 7300 mg/kg As based on analysis by ICP-OES. Both XRF instruments identified the three toxic elements, although the XOS prototype instrument had less bias (Pb 8%; Hg −36%; As 45%) compared to the Niton (Pb 51%; Hg −38%; As 78%). This is in accordance with the general trend for Hg of an absolute bias <50% for all the concentration ranges measured and with the general trend of higher absolute bias at As concentrations < 1%.

A third example is the Emperor's Tea Pill which is an HMP imported from China and labelled for 'natural balance'. Analysis by ICP-OES showed that it contains 4900 mg/kg Pb and 7100 mg/kg Hg. Both XRF instruments correctly identified the presence of Pb: XOS 2200 ± 200 mg/kg; Niton 4400 ± 50 mg/kg, and Hg: XOS 3900 ± 200 mg/kg; Niton 4000 ± 80 mg/kg when the sample was prepared in a powdered form.

The samples were re-analysed as whole tablets, using several layers of intact Emperor's Tea Pills placed in the sample cup, to explore the effect of sample preparation on performance. With this approach, Pb and Hg were detected on the XOS (680 ± 90 mg/kg Pb and 1010 ± 40 mg/kg Hg) and on the Niton (3400 ± 100 mg/kg Pb and 2700 ± 80 mg/kg Hg). They both demonstrated much poorer accuracy than when the sample was analysed in powdered form. Imprecision was also slightly poorer for whole tablets (up to 13% RSD) compared to powders (up to 10% RSD) for both XRF instruments. The poorer performance for whole tablets versus powdered samples was less pronounced for the Niton than the XOS prototype instrument. This may be due in part to the larger spot size of the Niton (8 mm), which is less affected by sample heterogeneity, compared with the smaller (<1 mm) spot of the XOS prototype. Nevertheless, each of the XRF instruments correctly identified very high levels of Pb and Hg in whole tablets, suggesting that either would be adequate for rapid screening of such products without the need for sample preparation.

Figure 4 shows difference plots for the elements Cd, Cu, Ba, Fe, Zn, and Mn in HMP, ES, CP powdered samples. The dashed lines denote an arbitrary performance
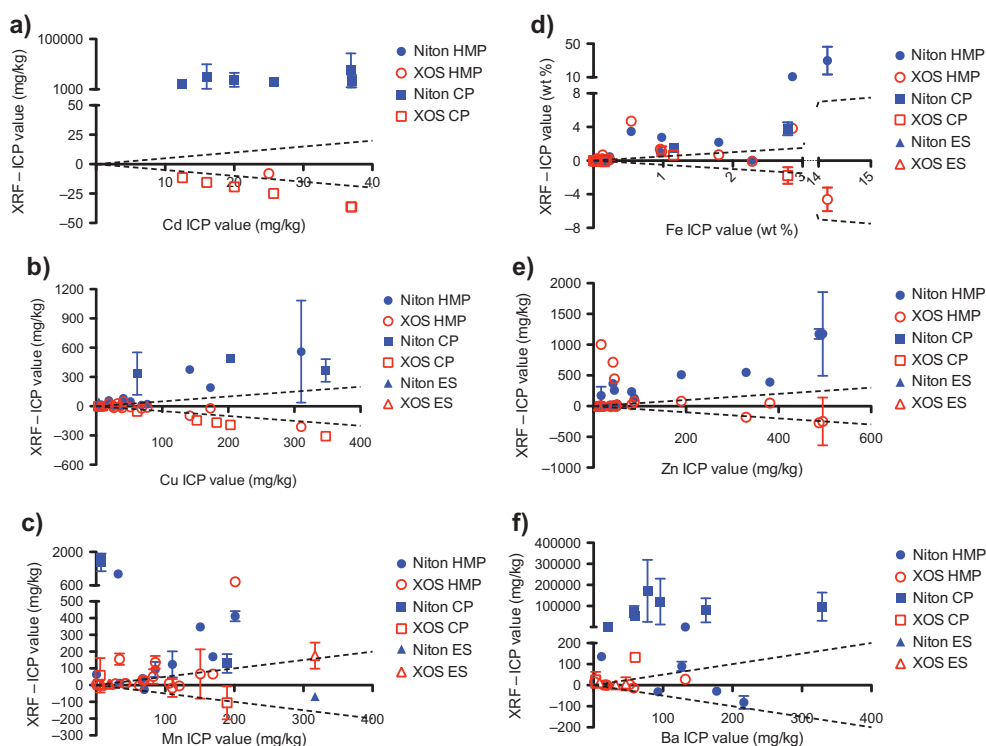

Figure 4. Difference plots (XRF – ICP-OES value) for Cd, Fe, Cu, Zn, Mn, and Ba in powdered samples measured with the XOS prototype and the Niton; XRF($n = 3$, error bars ±SD); the dashed lines indicate ±50% of reference value; HMP – herbal medicine product; ES – ethnic spice; CP – cosmetic product.

criterion of ±50% relative to ICP-OES. The elements were selected based on either their public health significance (Cd) or frequency of detection by XRF (Fe, Cu, Zn, Mn, and Ba).

In general, the Niton reports values for Cd, Cu, Fe, and Ba that are positively biased relative to ICP-OES. The XOS prototype data are less biased by comparison for Fe, Cu, and Zn. In the case of Mn, XRF performance is more complicated with several false positives errors noted for both the Niton and the XOS instruments. For the XOS prototype, this may be the result of disabling the lower energy beam at 7 keV, which may be more optimal for exciting the Mn Kα line.

For Cd, the XOS prototype instrument reported a negative bias that was proportional to the concentration range studied, while the Niton reported a large systematic positive bias that was >1000 mg/kg. These data underline the real challenges of measuring Cd in field-type samples by portable XRF, given the low energy of the Cd Lα line (3.133 keV), its low fluorescence yield, and a high spectral background in this region. Overall, Cd detection was poor for both XRF instruments, due in part to the low concentrations (≤37 mg/kg) present in these samples, and the technical challenges in measuring Cd by XRF using these instruments. However, the performance for Cd appeared better for the XOS prototype than for the Niton instrument. For example, Cd was detected with the XOS (17 ± 3 mg/kg) in the Emperor's Tea Pill but was reported as <LOD = 5 mg/kg by the Niton.

Of the samples analysed by ICP-OES, 63% (24/38) contained Pb, while 89% (34/38) contained As, Cd, Hg, or Pb. Of the contaminated products, 74% (25/34) were found to contain at least two of these toxic elements. Thus, while lead poisoning associated with use of HMPs is most often reported in case studies and remains the primary health concern, potential toxicity associated with As, Cd, or Hg exposure should also be considered for consumers using HMPs. While numerous products either did not have labelling in English or packaging was not available, one sample was labelled as 'lead-free' (defined on the product as <20 ppm), and three were marked with a claim of good manufacturing practice (GMP). The sample labelled as lead-free was found to contain Pb (~30 mg/kg), and each of the GMP-labelled samples contained detectable levels of Cd, Hg, or Pb.

The samples analysed in this study can be compared to elemental contaminant limits for dietary supplements (maximum intake of 10 g/day) suggested by the U.S. Pharmacopeia; 1.5 mg/kg As, 0.5 mg/kg Cd, 1 mg/kg Pb, and 1.5 mg/kg Hg [27]. For colour additives, As is typically permitted up to 3 mg/kg, Hg at 1 mg/kg, and Pb at 10–20 mg/kg dependent upon the colourant [28]. Since the MDLs of both the XOS prototype and the Niton are near or above these limits, it is unlikely that either instrument would be appropriate to determine compliance with regulatory limits. However, considerable time and cost savings, as well as increased screening rates, could be realised if either is employed as a tool to identify materials with potential toxicologically significant elemental content. Then a follow up study with accepted laboratory methods could be performed if either XRF instrument detects a potential problem.

3.4. *Study limitations*

Limitations exist in the sample preparation techniques used for this study. First, many of the HMPs analysed by ICP-OES were a sub-sample of the original product that was digested in their initial (e.g. tablet) form, rather than a digestion of the actual powdered sample measured by XRF. Therefore, the comparability of XRF and ICP-OES data could potentially be influenced by within-product variability. Analysis of the original tablets by ICP-OES was carried out to permit the calculation of the elemental content per tablet, and for direct comparison to measurement of the intact tablets by XRF (data not shown). None of the samples were dried prior to analysis, because drying would be difficult under field conditions, which was the intended purpose of the XOS instrumentation. Ideally, it might be useful to analyse these samples as wet and dry to determine what effect drying would have on their reported elemental composition by XRF. However, the contribution to overall uncertainty in the XRF results has been reported to be minimal for a residual moisture content up to 20% [29]. Several of the samples provided by the NYC DOHMH for use in this validation study were previously analysed for As, Hg, and Pb content by another laboratory, and those results were published elsewhere[4]. Moreover, most of the samples analysed in this study were received as sub-samples (i.e. from the same package). In some cases, samples were removed from an unopened package of the same lot, while in other cases they may have been from a different lot. HMPs are an example of products where there is a lack of homogeneity. Many are essentially 'hand-made' and do not have the uniformity characteristics usually associated with pharmaceutical grade dietary supplements and drugs. Hence, differences between tablets within the same lot are often very large. Despite this, it is notable that our ICP-OES results for Hg are generally higher (by as much as 75%) than those reported previously.[4] This discrepancy may warrant further investigations of the method used by the other laboratory, and its validation for these types of samples, as those details were not given in that report.

4. Conclusions

The performance (accuracy, precision, and robustness) of two field-portable XRF instruments, a prototype XOS instrument featuring DCC optics and a Niton XL3t analyser, were evaluated and compared to ICP-OES under laboratory conditions, for determination of multiple elements in HMPs and other ethnic (ES and CP) products. Both instruments performed adequately for the identification of contaminated HMPs and ethnic products that may pose a significant public health threat. Neither XRF instrument was sufficiently sensitive for quantifying major toxic contaminants below 15 mg/kg with good accuracy. Nonetheless, the real advantage to this type of XRF technology is its potential for portability, use on site and real-time analysis, as well as pre-screening samples prior to analysis by ICP-OES/MS. However, as designed, the XOS prototype instrument was not as portable or as easy to transport as was the Niton analyser. Further improvements in the design of the XOS instrument are warranted for future field applications. The results of this study highlight some of the challenges that may be encountered when using portable XRF instruments in the field, including issues related to sample preparation and the limitations of calibration and quantitation based on FP models. Users should be aware of the potential for misinterpreting results, especially for those samples that contain both As and Pb. The key

advantages of XRF over laboratory-based methods are that it is non-destructive, provides for rapid identification of multiple toxic elements at elevated levels, and can be used under field-based conditions by technicians with some basic training in analytical science.

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Disclosure statement

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