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Evaluation of a New Optic-Enabled Portable XRF Instrument for Measuring Toxic Metals/Metalloids in Consumer Goods and Cultural Products

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Abstract

X-ray fluorescence spectrometry (XRF) is a rapid, non-destructive multi-elemental analytical technique used for determining elemental contents ranging from percent down to the μg/g level. Although detection limits are much higher for XRF compared to other laboratory-based methods, such as inductively coupled plasma mass spectrometry (ICP-MS), ICP-optical emission spectrometry (OES) and atomic absorption spectrometry (AAS), its portability and ease of use makes it a valuable tool, especially for field-based studies. A growing necessity to monitor human exposure to toxic metals and metalloids in consumer goods, cultural products, foods and other sample types, and while performing the analysis *in situ* has led to several important developments in portable XRF technology. In this study, a new portable XRF analyzer based on the use of doubly curved crystal optics (HD Mobile®) was evaluated for detecting toxic elements in foods, medicines, cosmetics and spices used in many Asian communities. Two models of the HD Mobile® (a pre-production and a final production unit) were investigated. Performance parameters including accuracy, precision and detection limits were characterized in a laboratory setting using certified reference materials (CRMs) and standard solutions. Bias estimates for key elements of public health significance such as As, Cd, Hg and Pb ranged from −10% to 11% for the pre-production, and −14% to 16% for the final production model. Five archived public health samples including herbal medicine products, ethnic spices and cosmetic products were analyzed using both XRF instruments. There was good agreement between the pre-production and final production models for the four key elements, such that the data were judged to be fit-for-purpose for the majority of samples analyzed. Detection of the four key elements of interest using the HD Mobile® was confirmed using archived samples for which ICP-OES data were available based on digested sample materials. The HD Mobile® XRF units were shown to be suitable for rapid screening of samples likely to be encountered in field based studies.

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Keywords

X-ray fluorescence; lead; cadmium; arsenic; mercury; consumer goods; cultural products

Introduction

Exposure can be defined as the “contact between an agent and the visible exterior of a person (*e.g.*, skin and openings into the body)” [1]. Personal exposure measurements assess or estimate the level, frequency and time extent of the exposure and can be performed *directly* or *indirectly*. In the direct approach the level of exposure is determined on or within an individual (using a individual sampler or a biological marker); in the indirect approach the level of exposure is usually determined by models, questionnaires and environmental measurements, but not directly linked to the individual [2]. Collecting exposure data at an individual level allows us to understand the nature, frequency and the extent of possible exposures by identifying the sources and pathways of contamination. Personal exposure monitoring systems, like dosimeters (measuring ionization radiation), personal sampling pumps and filters (detecting airborne nanoscale materials) and personal aerosol badge monitors (detecting aerosol exposure) are commonly used in field analyses. However, these devices can be inaccurate, with poor detection limits and maybe difficult to apply to large study populations [2].

In the past decade, agencies such as the National Institutes of Health (NIH) have supported different projects to develop novel technologies to enhance personal exposure assessments [3] [4]. These projects have endeavored to develop tools to be used under the complex conditions that reflect ‘real world’ environments. One of the areas where there is a lack of personal exposure assessment devices is toxic metal/metalloid contaminants in consumer goods and cultural products. Non-essential metals, such as cadmium (Cd), mercury (Hg), and lead (Pb), and metalloids such as arsenic (As) can cause many adverse health effects. For example, Cd has been linked to Itai-itai disease (a combination of osteomalacia and osteoporosis), while Pb and Hg are both harmful to the nervous system. Exposure to inorganic As is known to cause certain types of skin cancer [5]. Even at low exposure levels, these elements are associated with more subtle toxic effects such as reduced cognitive functioning, lethargy and irritability [6]. The pathways for exposure to these contaminants include ingestion (food, herbal supplements, consumable liquids), dermal exposure (cosmetics and hygiene products) and inhalation (toxic fumes and particulate matter).

Recently, papers published on trace element contamination of foodstuffs, cosmetics and medicines have shown an increasing interest in X-ray fluorescence (XRF) as an analytical technique [7]. XRF spectrometry has the capability of simultaneous multi-elemental analysis with a wide dynamic concentration range from percent down to μg/g levels. Its non-destructive character preserves samples for further confirmatory analyses, if necessary. Another main advantage of XRF is the minimal sample preparation required and high sample throughput. This rapid screening technique minimizes considerably the time of analysis when compared with conventional techniques such as inductively coupled plasma mass spectrometry (ICP-MS) or inductively coupled plasma optical emission spectrometry

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(ICP-OES), which require time-consuming sample preparation procedures. XRF's simplicity, its lower cost and non-destructive analyses (when compared with ICP-MS, XRF can be 5 times cheaper) [8] makes it ideal technology for rapid screening of large numbers of samples. Several studies have used this non-destructive technique for screening a wide variety of samples pertaining to public health including: flour [9], seafood [10], Indian spices and ceremonial powders [11], FDA-regulated products [8], Ayurvedic medicines [12], face powders [13] and several other food and medicinal items [14]. A comprehensive discussion of consumer product regulations for metal contaminants is beyond the scope of this paper. Clearly, what constitutes "acceptable limits" for toxic elements will vary from one jurisdiction to the next, and by the type of consumer product (foods, pharmaceuticals, and cosmetics).

The versatility and broad range of applicability of XRF spectrometry have made it an indispensable analytical tool for field-portable applications. Portability is indeed one of the major advantages of XRF. For example, the possibility of bringing the instrument into people's homes and completing measurements *in situ* allows rapid on-site identification of products containing toxic elements and thus the possibility of providing results immediately. Ideally, the operator should be experienced in XRF spectra interpretation to use this portable instrumentation, particularly when measuring samples containing high concentrations of multiple elements with overlapping fluorescence lines. Commercial portable instruments use proprietary algorithms to estimate element concentrations. These results should always be confirmed by thorough analysis of the spectra in order to prevent reporting a result that originated from a peak misidentification by the software.

Because commercial portable XRFs are manufactured to accommodate several types of users, they have different measurement modes (plastic, metal, soil, glass, *etc*.) that are available for the user to choose, depending on the type of sample to be analyzed. A disadvantage is then the operator is limited to those modes, and all the restraints that come with them. Often portable XRF instrument only report a limited number of elements, which justifies the proposition that the operator should have spectra interpretation capabilities to be able to identify elements not reported by the selected mode. The accuracy of XRF also depends on the sample homogeneity, thickness and flatness towards the beam. Preparing a sample with appropriate characteristics for accurate quantification may require extra time and care if the XRF is used for purposes other than screening.

Besides these drawbacks that can be easily overcome, the main limitation of portable XRF is the high detection limit, in the μg/g range for toxic elements like As, Cd, Hg and Pb, compared to ng/g and pg/g of techniques like ICP-MS. Yet, this limitation may not be so critical where the overall goal is to screen samples for high levels of contamination for those key elements, and as quickly as possible. With the purpose of improving the detection limits, several important developments in hardware and the introduction of X-ray optics in these systems have enhanced the performance of portable XRF and even increased their portability.

The instrument evaluated in this study, the HD Mobile®, was developed by X-Ray Optical Systems (XOS), of East Greenbush, NY and is based on monochromatic micro-XRF. It uses

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a “High Definition” XRF (HDXRF) technique that includes Doubly Curved Crystal (DCC) optics to enhance measurement intensities [15]. Furthermore, it is housed in a unique, self-contained case designed for transportation to and use in the field. The primary goal of this study was to validate a pre-production and a final production unit of the instrument HD Mobile®, for assessing environmental exposure to toxic metals through food, cosmetics, medicines and personal care products. A validation study was carried out using a group of certified reference materials and standard solutions to assess accuracy, precision and detection limits. Archived samples including herbal medicines, ethnic spices and cosmetic products were also analyzed by the HDXRF units to assess instrument performances when dealing with “real world” samples.

Experimental

Instrumentation

All XRF measurements were performed using the HD Mobile® Analyzer (X-Ray Optical Systems, East Greenbush, NY). The HD Mobile® is the product of several years of research and development at XOS that began as an early prototype “Personal Environmental Analyzer“ and which was fully evaluated as described previously [16]. The lessons learned from the early prototype evaluation [16] were implemented in the HD Mobile® instruments that were used here. In this study, the analytical performance of the HD Mobile® was assessed using two instruments: a pre-production unit that was loaned by XOS (Fig. 1a), and a final production (Fig. 1b) unit that was purchased from XOS.

The HD Mobile® is equipped with a low-power (5–10 W) X-Ray tube (Mo-anode) excitation source. The excitation beam is focused onto the target using proprietary DCC optics, yielding a spot size of 1-mm. The DCC optic provides monochromatic excitation at three energies: 6.4 keV, 17.4 keV and 34 keV. Capturing the divergent X-ray beam and redirecting the subsequent monochromatic energies into an intense focused beam on the sample’s surface enhances the count rate of the detected peaks. This enhancement in the peak intensities allows lower power sources to be used and reduces scattering background under the characteristic X-ray peaks, which in turn enhances elemental detection limits and shortens measurement times. The fluorescent photons are collected by a silicon drift detector (SDD).

The HD Mobile® can be operated in either a “screening” mode or a “quantifying” mode – the latter was used throughout for this work. A number of matrices can be selected for sample analysis including: plastic, metal, wood, glass, rubber, leather, bulk paint, textiles and trace paint. In this study, the plastic mode was selected as most suitable for our evaluation purposes based on prior experience with XOS’ calibration protocols for the HDXRF technology [16]. In plastic mode the measurement time is fixed at approximately 3 minutes.

Both the pre-production and final production models can be operated as a handheld device or as an integrated system within the case. In this study, both were operated within their self-contained cases. The case dimensions are approximately 55 (H)×42 (W)×27 (D) cm for the pre-production and 63 (H)×51 (W)×30 (D) cm for the final production instrument and the

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whole system weighs 24 kg (~ 53 lbs) for both models. The X-ray analyzer is secured in a stand such that the sample is analyzed within a shielded chamber. The instrument is coupled to a human interface module (HIM) that provides data acquisition and instrument control. The HD Mobile® is equipped with a CCD camera to facilitate sample positioning and enable a unique image to be stored along with the analytical report. When analyzing samples on the final production instrument, a polypropylene thin film (SpectroMembrane® Prolene® Thin Film®, Chemplex Industries, Palm City, FL) was placed over the beam tip to prevent external contamination from sample leakage. To accommodate this, a removable sample tray was installed over the X-ray tip. This represented an improvement over the pre-production model.

For quantification, the HD Mobile® is equipped with a proprietary software – "solver", that fits the X-Ray spectrum, and calculates analyte concentrations based on fundamental parameters method [17, 18]. Prior to collecting the study data presented here, we provided some preliminary data (not shown here) to the instrument manufacturer (XOS) to optimize their solver software for quantifying toxic elements in biological matrices.

Certified reference materials

Certified reference materials (CRM) were obtained from: (a) International Atomic Energy Agency (IAEA, Vienna, Austria), IAEA-413 Major, Minor, and Trace Elements in Algae; (b) National Institute of Standards and Technology (NIST, Gaithersburg, MD), NIST Standard Reference Material (SRM) 1571 Orchard Leaves and NIST SRM 2976 Mussel Tissue (Trace elements and methylmercury); (c) National Research Council of Canada (NRC, Ottawa, Canada), NRC TORT-2 Lobster Hepatopancreas RM for Trace Metals and NRC DORM-2 Dogfish Muscle CRM for Trace Metals; and (d) Institute of Reference Materials and Measurements (IRMM, Geel, Belgium), IRMM CRM BCR®-627 Tuna Fish Tissue, and IRMM ERM-CE464 Tuna Fish. The CRMs were analyzed to assess HD Mobile® accuracy and precision for solids.

Aqueous calibration standards and archived proficiency testing samples

Aqueous calibration standards were analyzed to assess linearity, sensitivity, and check the deconvolution of peaks by the solver. Single element standards for As, Cd, Hg, and Pb were prepared in concentrations of 10, 50, 100, 500, 1000, 5000, and 10000 μg/mL from 10000 μg/mL stock standards (Accustandard, New Haven, CT and Ricca Chemical, Arlington, TX). Multi-element solutions containing As, Cd, Hg, and Pb were prepared at 10, 50, 100, 500, 1000, and 2000 μg/mL from the single element 10000 μg/mL stock standards. Multi-element standards containing 20 elements (Accustandard) at 10 μg/mL and 50 μg/mL were spiked with Hg in the same concentrations and analyzed for the determination of the limits of detection.

In addition to the calibration standards, archived proficiency testing (PT) samples for trace elements in water were obtained from the New York State Department of Health's (NYS DOH) Environmental Laboratory Accreditation Program (ELAP). These independently validated ELAP PT samples were analyzed to assess HD Mobile® performance for Non-potable Water (NW Metals I and II, #5511A) and Potable Water (PW Metals, #5706). Each

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PT sample had a certificate that included an assigned target value, with lower and upper acceptable performance limits for select trace elements.

Archived cultural products

A number of archived cultural products, received as part of previous public health investigations, were available to this project for validation proposes. Powdered samples were simply poured into an XRF cup and analyzed. Pills and tablets were crushed and ground, using a pestle, into a coarse powder able to pass through a 2-mm (USS#10) sieve. Approximately 2–6 g of sample was transferred into an XRF cup (32 mm (OD)×24 mm (H), Premier Lab Supply, Port St. Lucie, FL) sealed at the bottom with a 4-μm Ultralene window-film, for analysis. The XRF cup was always filled to approximately ½ full, equivalent to ~1 cm thickness, which ensured infinite path thickness. Each sample was measured in three different spots.

HD Mobile® results were compared to data collected by ICP-OES. Sample treatment for ICP-OES analysis is described in detail elsewhere [16]. Briefly, all samples were acid digested using a modified procedure based on EPA Method 3050B that included 100 μL of 500 μg/L Au solution (to prevent Hg volatilization). The samples analyzed included: (a) Hashmi Surma Special personal care product from India, a fine black powder of lead sulfite used as a cosmetic for the eyelids; (b) Turmeric spice from India, used for cooking; (c) Suketu cultural medicine from India, used as a remedy for deworming, abdominal cramps and pain due to infection; (d) Mahayogaraj Guggulu cultural medicine from India, used for treatment for rheumatic pain and (e) Emperor's Tea Pill cultural medicine from China, labeled for "natural balance".

Optimization and validation study design

A study was conducted in order to determine the optimal sample volume for analyzing liquid samples when using XRF micro polyethylene 10 mL sample cups (31 mm (OD) × 21 mm (H), Premier Lab Supply, Port St Lucie, FL). A solution containing 100 μg/mL each of As, Cd, Hg, and Pb was pipetted at volumes of 0.75, 1.0, 2.0, 3.0, and 3.5 mL into different sample cups and analyzed. To determine the optimal mass (which is related to thickness) for analyzing solid and powdered samples, the IAEA-413 Algae CRM was weighed into different sample cups at masses of 0.1668, 0.3406, 0.5697, 0.8180, and 1.008 g and analyzed. The optimal volume and mass parameters were determined based on which gave the most accurate results with respect to the known/certified values.

To check the instrument for background contamination, a liquid (DI water) and a solid (boric acid 99.9995% – Alfa AESAR, Ward Hill, MA) blank were measured. Instrument sensitivity (counts/ (μg/mL)) was determined by recording the counts for each single-element aqueous standard of As, Cd, Hg, and Pb at concentrations of 0, 10, 50, 100, 500, 1000, 5000, and 10000 μg/mL. A second-order polynomial regression was fit to the data. Measured concentrations from these same standards were also used to assess the response of the instrument as a function of concentration of single-element solutions. The same assessment was completed with a solution containing As, Cd, Hg, and Pb together at concentrations of 0, 10, 50, 100, 500, 1000, and 2000 μg/mL, in order to study the

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performance of the instrument when several peaks of interest are simultaneously present in the sample. This concentration range was limited by the original 10000-μg/mL single-element standard solutions, which were combined to prepare the four-element solution. Linear regression lines were fit to the single and four-element standard data. For the volume, mass, sensitivity, and instrument response studies, each sample was measured in triplicate at the same spot on a single day in order to obtain the mean and standard deviation.

The accuracy of the instrument for aqueous samples was determined through the measurement of the single and four-element standards solutions, and through the NYS ELAP PT NW Metals I and II and PW Metals. These samples were measured in triplicate in the same spot on a single day. The bias between the measured and PT program target values were calculated, as well as a percent difference between the pre-production and final production instruments.

For solid matrices, accuracy was assessed through the analysis of the following CRMs: (a) IAEA-413 Algae, (b) NIST SRM 1571 Orchard Leaves, (c) NIST SRM 2976 Mussel Tissue, (d) NRC TORT-2 Lobster Hepatopancreas, (e) NRC DORM-2 Dogfish Muscle, (f) IRMM CRM BCR®-627 Tuna Fish Tissue, and (g) IRMM ERM-CE464 Tuna Fish. These reference materials were selected due to their light matrix and similarity to many of the sample matrices of interest. Each CRM was analyzed in triplicate and in the same spot per day over five days. Inter-day precision was calculated based on these measurements. Intraday precision was also assessed by analyzing each CRM ten times in the same spot on one day. The bias between the measured and certified values was calculated, as well as a percent difference between the pre-production and final production instruments.

The performance of the pre-production and final production models as assessed using “real” nonideal samples, archived from previous health investigations. These samples had been analyzed by ICPOES [16] previously and included: (a) Hashmi Surma Special, (b) Turmeric, (c) Suketu, (d) Mahayogaraj Guggulu, and (e) Emperor’s Tea Pill. Each sample was measured in three different spots in order to capture sample inhomogeneity, but only on a single day. The means and standard deviations of the two XRF instruments were compared with one another and with the ICP-OES measured value.

Final XRF combined standard uncertainties (u_c) were calculated for all results by the following equation:

$$u_c = \sqrt{\mathrm{SD}^2 + (u_{\mathrm{FP}})^2} \quad \text{Equation 1}$$

where SD is the standard deviation of repeated measurements, and u_{FP} is the maximum uncertainty that is reported by the manufacturer’s FP algorithm. Equation 1 combines two components of uncertainty arising from peak area measurements (FP), with repeated sampling measurements, using the root-sum-of-squares method [19, 20].

Limits of detection

The limit of detection (LOD) was calculated using two different approaches: the IUPAC recommends that the LOD be based on at least 6 independent determinations of the

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concentration of the analyte of interest in a matrix blank or low-level material, and approximate detection limit is then calculated as three times that precision estimate, *i.e.*, 3×SD [21]. However, in conventional XRF practice, the LOD is typically calculated based on the number of counts observed for the background and peak signal, with the following equation [18]:

$$\mathrm{LOD} = C_i * 3 \frac{\sqrt{(N_\mathrm{b})}}{N_\mathrm{p}} \quad \text{Equation 2}$$

where C_i is the standard analyte concentration, N_b is the number of counts in the background and N_p is the number of counts in the peak area.

In this study, the “IUPAC” LOD for aqueous solutions was calculated as 3×SD of ten replicate XRF measurements of a 10-μg/mL multi-element solution. Use of a 10-μg/mL solution, rather than an aqueous blank solution, is necessary to achieve measurable signals close to the LOD and to avoid having the FP algorithm report results as below the detection limit. For solid matrices, the “IUPAC” LOD was calculated as 3×SD of ten replicate XRF measurements of a powdered CRM having the lowest detectable concentration (based on the instrument-software reported value) for each element from the available CRMs. For comparison, the “conventional XRF” LOD was also calculated using the 10-μg/mL multi-element solution and the powdered CRM with the lowest concentration of each element from the available CRMs.

Results and Discussion

Our early evaluation data for the pre-production instrument were shared with XOS engineering staff, who were able to implement incremental improvements to their proprietary algorithms software, the “solver”, and which is used to calculate reported concentrations. To ensure accuracy for key elements in the various matrices, updated solvers were checked by analyzing the CRMs. The final sample volume or mass were optimized, as described below, and key analytical performance parameters (sensitivity, instrument response, limit of detection, accuracy) were characterized for both the pre-production and the final production units, based on the final version of the solver installed by XOS.

Volume

The optimum sample volume for liquids was investigated by analyzing an aqueous standard solution spiked with 100 μg/mL As, Cd, Hg and Pb. The recovered value (± *u*) as reported by the instrument software served as the performance indicator. In general, there was little difference between the five different sample (liquid) volumes investigated (0.75, 1.0, 2.0, 3.0, and 3.5 mL), such that 3.0 was selected for all subsequent measurements. The data for As, Cd, Hg and Pb show some variation between elements, but average values were all close to ±10%. There was a shift in bias between the pre- and final production models, with a small (≤10%) negative bias for the pre-production model, and a positive bias for the final production model. Notably, the uncertainty for Cd far exceeded that for the other three, but this is not unexpected given the challenges of determining Cd by XRF (see below). The data are summarized in Fig. 2, where (irrespective of volume) only the minimum and maximum

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values are shown for clarity. Since performance was typically ±10%, the performance was judged fit-for-purpose.

Mass

The optimum sample mass was determined by analyzing a CRM (IAEA-413 Algae) for As, Cd, Hg and Pb on both models. Fig. 3 shows the values found on the pre-production and final production model for each of the four elements at five different masses, ranging from ~0.17 to ~1.0 g. The dashed lines represent the certified (As, Cd, Pb) or reference value (Hg) assigned for the CRM. With the possible exception of Cd, sample mass had little influence on the reported values. However, Hg exhibited a systematic bias that ranged from 7 to 13%. Between-sample variation was within ±3% for Pb, ±2% for As and ±4% for Hg, for both units, regardless of sample mass used. The data in Fig. 3 shows some overall improvement in performance for the final production instrument, including better accuracy for Pb and better within-sample precision for As.

It is clear that, for Cd, the lowest mass (0.1668 g) resulted in a higher bias compared to the other masses. This means that sample thickness becomes negligible above 0.1668 g, *i.e.* the fluorescent X-rays produced at certain depths can no longer reach the detector. While the minimum mass required to achieve infinite thickness (with these specific XRF cups) is ~0.167 g, at least 0.3 g of sample is preferred to avoid a negative bias for Cd, and ensure infinite path thickness for As, Hg, Pb and Cd. A mass of 0.3 g is equivalent to filling the cup to ~ 0.5 cm. When sample sizes are not limited, the XRF cups should be half filled to compensate for differences in sample matrices and densities.

Blanks

Two blanks, a liquid (DI water) and a solid (boric acid), were analyzed on both units as part of a quality control protocol. Both instruments reported an unexpected value for Sn: 5–10 μg/mL for DI; and 5–10 μg/g for boric acid. Further investigation of the raw spectra indicated the possible cause to be a poor fit (Fig. 4a). This artifact would be troublesome where Sn measurements are of interest. In addition to reporting values for Sn, the pre-production unit also reported values for Sb: 20–30 μg/mL for DI; and 20–30 μg/g for boric acid. Again, further investigation of the raw spectra indicated a poor fit (Fig. 4a), but this problem was not observed with the final production unit. The Sb "signal" was investigated further using a set of Sb standard solutions, ranging from 10 μg/mL to 10,000 μg/mL (Accustandard). At concentrations above 500 μg/mL, the 20–30 μg/mL "Sb artifact" was <10%. However, at lower concentrations the "Sb artifact" was consistently 20–30 μg/mL, which necessitated excluding Sb measurements in this study. While the root cause of the "Sb artifact" was not definitively established for the pre-production instrument, the problem was subsequently resolved for the final production model. While the "blank" reported values for Sn and Sb were associated with poor fitting of the raw spectra, additional peaks were clearly identified in the raw spectra for both instruments as Ni(K_α) (7.47 keV) and Ni(K_β) (8.26 keV), and are likely due to some internal contamination (Fig. 4b). The XOS solver was able to account for this internal background signal when reporting results for Ni, such that Ni was reported as "not detected" in the blanks.

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Instrument response – sensitivity

Instrument sensitivity is shown in Fig. 5 for (a) the pre-production and (b) final production instruments as plots of counts versus aqueous standard concentration. The y-axis values represent triplicate measurements of the instrument's response. The fit is non-linear, and follows a quadratic function. Arsenic has better sensitivity followed by Pb, Hg and finally Cd, with considerably less sensitivity. XRF sensitivity depends on a number of factors, including X-ray source power, detector efficiency, measurement time, sample matrix, and the element of interest. Use of DCC optics significantly increases sensitivity for some elements while allowing a high flux density excitation beam to interact with the sample. Poor sensitivity for Cd is partly due to the increased background signal that occurs with the high-energy excitation beam, which is required to excite Cd at 23.11 keV (K_α) and 26.08 keV (K_β). In addition, the latter is complicated by an interference from the K_α line from Sb at 26.27 keV.

Instrument performance – linearity of FP reported concentrations

The linearity of FP reported concentration values are summarized in Table 1 based on analysis of both single element and multi-elemental standard calibration solutions. Simple linear regression fits were performed and, with the exception of As on the final production model, all had an R^2 >0.995, indicating good linearity over the concentration range studied. In general, FP model successfully corrects non-linearity in the instrument response, as shown by the data in Table 1. For As in a multi-element standard solution, there could be a deconvolution issue at high concentrations in the presence of Pb. From a practical XRF perspective, the slope from each linear fit should ideally be within ±10% of 1.00, and in general this holds for all elements except for Hg in a single element standard. The extended concentration range (up to 10,000 μg/mL) that is possible with single element standards forces the slope to exceed 10%, but only by 1–2%. Differences between the slopes for respective elements in single versus multi-element solutions are more likely due to the extended calibration range for the former, although some inter-element effects cannot be ruled out.

Instrument performance - Limit of Detection

The LODs were calculated using two approaches: (a) according to IUPAC recommendations [21] and (b) following the conventional XRF practice [18]. A 10-μg/mL multi-elemental solution was used for LOD determination for both approaches on both instruments (Table 2). These LOD's are based on simple aqueous standard solutions and are equivalent to an instrumental detection limit (IDL), reported for other analytical techniques. The characteristic lines used to calculate the LODs according to Equation 1 were based the K_α lines for all elements, except Pb and Hg, for which L_α line was used due to the higher atomic numbers for those two elements. LODs were typically 1–4 μg/mL for most elements, except for Cd, Sn, and Sb, which ranged from 5 to 15 μg/mL. The poorer LODs for these three elements are due to the poorer sensitivities using the high-energy excitation beam, as explained above for Cd.

It is interesting to note that there is good agreement between the LODs calculated based on the IUPAC procedure and those based XRF conventional practice for most elements, except

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Sb and Sn. The discrepancies noted for Sb and Sn LODs are most likely due to the issue of poor fitting and/or internal contamination for these elements as explained above. When using the IUPAC approach, where the SD of repeated measurements is multiplied by an appropriate coverage factor, the LOD can become inflated if the reported concentration is highly elevated. In the case of Sb, the LOD was re-calculated using a 50 μg/mL standard on the final production instrument, and found to be 33 μg/mL based on IUPAC and 14 μg/mL based on XRF practice (Table 2).

Method LODs were calculated based on 6 powdered reference materials, using both the IUPAC recommendation and the XRF practice. Table 3 shows the data for both instruments, and represents “bona fide” estimates, of the LOD based on sample matrices such as food. The characteristic X-ray lines used to calculate the LODs according to Equation 1 were K_α for all elements except Pb and Hg due to their higher atomic number, where the L_β and L_α were used, respectively. The reason why Pb L_β (12.61 keV) was chosen instead of L_α (10.55 keV) is that the reference material used for this determination (SRM 2976 Mussel Tissue) contains As at an order of magnitude greater than Pb. Knowing that the As K_α (10.53 keV) and the Pb L_α (10.55 keV) lines overlap, the Pb L_β line (12.61 keV) was used instead. Method LODs were typically 1–2 μg/g for As, Se, Pb, Zn, Cu, and Hg, and up to 5 μg/g for Mn and Sr. Poorer LODs (9–11 μg/g) were evident for Ni, Fe, Cr, and Cd (as expected). It is interesting to note that many of the method LODs (As, Pb, Hg, Cu, Zn, and Se) were within 1–2 μg/g of the value determined using aqueous standards. For the remaining elements, method LODs were slightly poorer. These data show that this XRF instrumentation is capable of maintaining adequate sensitivity and precision, even for complex matrices. There was good agreement between the IUPAC and XRF approaches to calculating method LODs for all elements except perhaps for Ni, Cr and Fe, where small discrepancies on the order of 3–6 μg/g were noted. As noted above, IUPAC-calculated LODs may be higher, when the endogenous concentration is elevated.

The XOS HD Mobile® Analyzer is not the only portable XRF analyzer available for field type studies. Several manufacturers (e.g., Thermo Scientific Niton™, Olympus/Innov-X, Bruker, Oxford Instruments, etc.) market portable analyzers based on Energy Dispersive XRF with either X-ray tube or radioisotope excitation, and slits/filters to select the excitation energy. While a comprehensive comparison to other XRF systems is beyond the scope of the current study, a previous study from our laboratory compared the Thermo Niton XL3t GOLDD to a different prototype instrument that also used the HDXRF technique with DCC optics [16]. In that study, it was reported that the HDXRF yielded lower method LODs compared to the Niton.

ELAP Proficiency Testing Samples

Table 4 shows performance data for two NYS DOH ELAP PT water samples that were analyzed on both instruments. A number of elements were not detectable in these water samples: Al and V (low fluorescence yield), Ba (low energy L lines), Tl, Mo and U (not reported in “plastic mode” on these instruments). The data for the NW (non potable water) sample shows an improvement in performance for the final production instrument compared to pre-production model, with all but one parameter (Sr) meeting the ELAP quality

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specifications (±3SD). For the PW (potable water) sample, all but two parameters (Fe and Ni) measured on the final production model met the ELAP quality specifications (±2SD). While Fe and Ni measured in PW by HDXRF were outside of the acceptable range expected for PW with EPA approved methods of analysis, *e.g.*, ICP-MS, the XRF bias was less than 30%. The large positive bias for Sb reflects the poor spectral fitting reported above for the pre-production instrument. Performance for the pre-production model was noticeably poorer compared to the final production model, with seven unsatisfactory parameters for NW and five unsatisfactory parameters for PW. The slightly better performance for the final production model reflects ongoing efforts to improve the technology further, although both instruments may be considered “fit for purpose” for field-based studies, and both are still in reasonably agreement with each other.

Solid certified reference materials

Table 5 shows the results obtained from the analysis of seven CRMs. For most elements detected, the absolute bias (measured relative to assigned CRM value) was less than 15% for both the pre-production (69% of reported values) and final production instruments (77% of reported values). The percent reported values that were within ± 30% improves to 92% and 94% for the pre-production and final production instruments, respectively, which is quite significant for portable XRF technology. For public health purposes, the more significant contaminants (Pb, Cd, Hg and As) performed well within ±15% bias, while Fe and Cu were typically better than 33%, and inter-instrument agreement was better than 20%. The lighter mass elements detected and reported by the HD Mobile® (S, Cl, K and Ca) are not major issues for public health purposes. While there was a 25% negative bias reported for Cr when analyzing the DORM-2 Dogfish Muscle on the pre-production instrument, the relative uncertainty (24%) of the latter may render this insignificant, and the magnitude was absent on the final instrument. Between-day imprecision (defined as the relative uncertainty, %*u* in Table 5) was better than 15% for most measurements on the pre-production (>65%) and final production (>72%) instruments. With-day imprecision, assessed by analyzing each CRM ten times in the same spot on a single day (data not shown), was slightly better, with more than 87% of measurements better than 15% relative uncertainty on both instruments.

The availability of these CRMs provided an opportunity to evaluate the HD Mobile® performance for toxic elements in biological matrices. The paucity of CRMs certified for toxic elements in cosmetic and pharmaceutical matrices is a limitation in these types of studies, including this study. The data presented here for biological CRMs may well be generalizable to lower concentrations in cosmetics, and other matrices. However, future studies are warranted as such CRMs become generally available.

Analysis of archived cultural products

Fig. 6 compares XRF-measured values for As, Cd, Hg, or Pb obtained on samples archived from previous public health investigations with informational values previously reported by ICP-OES [16], or that were obtained from literature sources. Archived samples included (a) Hashmi Surma Special, (b) Turmeric, (c) Suketu, (d) Mahayogaraj Guggulu, and (e) Emperor’s Tea Pill. The cosmetic powder Hashmi Surma Special (Fig. 6a) is well known to be almost all “galena”, *i.e.*, PbS. Both HD Mobile® instruments report a mass fraction that is

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within 10% of literature values for Pb reported in Surma cosmetics (~88% by weight) [22]. Arsenic was not detected by XRF although analysis by ICP-OES indicated a value of 3 μg/g. Fig. 6b shows that Pb was detected by both instruments in the powdered spice "Tumeric" at ~0.25%, which is with 10% of the value obtained by ICP-OES. Analyses by ICP-OES also indicated Hg present in this sample at 1.2 μg/g, but this was not detected by XRF (LOD = 1–2 μg/g). Fig. 6c shows the data for As and Hg in Suketu, which was analyzed as a crushed pill, exhibiting a discrepancy of almost 30% for the former between the two XRF instruments. Lack of sample homogeneity (crushed pill) might explain this discrepancy, since three different spots of the sample were measured. In fact, the fixed spot size diameter of 1 mm for the HD Mobile® may be a possible limitation for inhomogeneous test samples when compared to other portable XRF analyzers that allow a larger spot size. By contrast, the agreement for Hg (at ~4% by weight) was reasonable between the two instruments, although the ~30% negative bias relative to ICP-OES (~6% by weight) suggests some further optimization might be warranted with the HD Mobile® solver. Regardless, the amount reported by XRF would still trigger a follow up from a public health perspective. Lead was not detected by XRF (possible due to high levels of Hg and/or to the presence As) even though a small amount (3 μg/g) was found by ICP-OES.

While the results are acceptable for samples (a) and (b), the remaining samples (c), (d), and (e), analyzed as crushed pills had worse performance. Mahayogaraj Guggulu was analyzed for As, Hg and Pb on both XRF instruments since elevated levels (% by weight) had been previously reported by ICP-OES [16]. While both instruments were capable of detecting these elements, the pre-production model exhibited large relative uncertainties, which appear to have been addressed in the final production model. The exact source of the larger uncertainty is unknown but may be a function of the heterogeneous nature of samples analyzed. However, the improved uncertainty in the final production model is offset by difficulty de-convoluting the signal for As K_α (10.53 keV) line from the Pb L_α (10.55 keV) line, when they are both present at high levels. This issue is also evident in the linearity data shown in Table 1, and has been discussed previously in the XRF literature [23]. Surprisingly, both XRF instruments reported elevated values of Cd (100–250 μg/g) for Mahayogaraj Guggulu, while Cd was not detectable by ICPOES. The large relative uncertainties (50–150% *u*) associated with the XRF results indicate that the data are unreliable.

Analysis of the Emperor's Tea Pill (Fig. 6e) for Cd, Hg and Pb showed good agreement between the two XRF instruments, but mixed results for agreement between XRF and ICP-OES. Values by XRF for Cd were within 25% of those found by ICP-OES, at the 25-μg/g level. By contrast, values for Hg and Pb, were low biased on both instruments: −46% and −49% for the pre-production and final production units, respectively, while for Pb the bias was −53% and −54%, respectively. While the magnitude of the negative bias may be relatively large, the amount of Hg and Pb present is so high (0.7% and 0.5%, respectively), that the XRF reported values (0.3% and 0.2%, respectively) can be considered "fit for purpose".

While the results for powdered samples (a) and (b) are acceptable, samples (c), (d), and (e), which were analyzed as crushed pills, had somewhat poorer performance. It is important to

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note that the sample regions analyzed by both ICP-OES and XRF were not exactly the same, so some differences between informational and the XRF-measured values might be expected, due to sample inhomogeneity, which is a particular problem for the pellet/tablet samples.

Conclusions

Two portable HD Mobile® XRF instruments were fully investigated and their performance validated for the analysis of cultural products, cosmetics and medicine samples using the instruments' "plastic" calibration mode. The minimum mass and the optimum range for sample volume were determined. Two blank samples were analyzed on both instruments and poor spectral fitting and/or internal contamination from Sb, Sn and Ni were identified. Sensitivity and instrument response characteristics were determined for As, Pb, Hg and Cd. While sensitivity is much poorer for Cd, the instrument response was linear for As, Cd, Hg and Pb in aqueous solutions, up to 10,000 μg/mL based on single element standard solutions, and up to 2,000 μg/mL for multi-element standard solutions. There was good agreement between the IUPAC and XRF conventional approaches to determining the LOD based on analysis of liquid and solid sample matrices. For those toxic elements of most concern from an environmental health perspective, LODs based on solid matrices for As, Pb, Hg and Cd were 1 μg/g for As and Pb, 1–2 μg/g for Hg, and and 9–11 μg/g dry wt for Cd.

XRF accuracy was assessed by analyzing archived PT water samples from the NYS DOH ELAP, along with seven biological CRMs from different sources. In general, the final production instrument demonstrated improved accuracy for all elements detected, although the agreement between the two instruments was good nonetheless. Analytical bias for As, Cd, Pb and Hg based on analysis CRMs ranged from −10 to +11% on the HD Mobile® pre-production instrument, and from −14 to +16% for the final production instrument (excluding those cases where the assigned value was close to the LOD). Five archived samples of cultural cosmetics, foods and medicines that were previously analyzed by ICP-OES, were also analyzed by both XRF instruments. The results show performance for both XRF units was better for powdered samples than crushed pills. Although quantification was matrix and element dependent, the HD Mobile® was able to identify correctly the presence of toxic elements in archived samples, with reasonable confidence for field-based measurements and good agreement between the two units.

Ideally, XRF performs best with solid samples, of "infinite" thickness and with smooth surfaces. But this is often difficult or impossible to achieve under field conditions, so some compromise is necessary. The archived samples represent a range of solids, powders, liquids and creams encountered in public health investigations, some with irregular surface features and with heterogeneous elemental distribution. Use of the fundamental parameters calibration model in these portable XRF instruments is based on ideal samples, such as CRMs, which are homogeneous and flat. Due to this, expectations for XRF accuracy and repeatability under field conditions will need to be realistic, relative to laboratory based methods (such as ICP-OES or ICP-MS), recognizing all analytical techniques have their limitations.

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References

1. EPA, Exposure Assessment in: Environmental Protection Agency.
2. Monn C. Exposure assessment of air pollutants: a review on spatial heterogeneity and indoor/outdoor/personal exposure to suspended particulate matter, nitrogen dioxide and ozone. Atmospheric Environment. 2001; 35:1–32.
3. NIHRFA, Environmental Sensors for Personal Exposure Assessment (SBIR [R43/R44]), in, NIH. 2007.
4. NIHRFA, Validation and Field Testing of New Tools for Characterizing the Personal Environment [R01], in, NIH. 2010.
5. Jarup L. Hazards of heavy metal contamination. British Medical Bulletin. 2003; 68:167–182. [PubMed: 14757716]
6. Friis, RH. Essentials of Environmental Health. 2nd. Sudbury, MA: Jones & Barlett Learning; 2012.
7. West M, Ellis AT, Potts PJ, Streli C, Vanhoof C, Wobrauschek P. Atomic Spectrometry Update - a review of advances in X-ray fluorescence spectrometry and their applications. Journal of Analytical Atomic Spectrometry. 2015; 30:1839–1889. 2015.
8. Palmer PT, Jacobs R, Baker PE, Ferguson K, Webber S. Use of field-portable XRF analyzers for rapid screening of toxic elements in fda-regulated products. Journal of Agricultural and Food Chemistry. 2009; 57:2605–2613. [PubMed: 19334748]
9. Ida H, Kawai J. Analysis of wrapped or cased object by a hand-held X-ray fluorescence spectrometer. Forensic Science International. 2005; 151:267–272. [PubMed: 15939161]
10. Mohapatra A, Rautray TR, Vijayan V, Mohanty RK, Dey SK. Trace elemental characterization of some food crustacean tissue samples by EDXRF technique. Aquaculture. 2007; 270:552–558.
11. Lin CG, Schaider LA, Brabander DJ, Woolf AD. Pediatric lead exposure from Imported indian spices and cultural powders. Pediatrics. 2010; 125:e828–e835. [PubMed: 20231190]
12. Saper RB, Kales SN, Paquin J, Burns MJ, Eisenberg DM, Davis RB, Phillips RS. Heavy metal content of Ayurvedic herbal medicine products. JAMA - Journal of the American Medical Association. 2004; 292:2868–2873. [PubMed: 15598918]
13. Kulikov E, Latham K, Adams MJ. Classification and discrimination of some cosmetic face powders using XRF spectrometry with chemometric data analysis. X-Ray Spectrometry. 2012; 41:410–415.
14. Reames G, Charlton V. Lead detection in food, medicinal, and ceremonial items using a portable X-Ray Fluorescence (XRF) instrument. Journal of Environmental Health. 2013; 75:16–20. [PubMed: 23397645]
15. Chen Z, Gibson WM. Doubly curved crystal (DCC) X-ray optics and applications. Powder Diffraction. 2002; 17:99–103.
16. McIntosh K, Guimarães D, Cusak M, Vershinin A, Zewu C, Yang K, Parsons PJ. Evaluation of portable XRF instrumentation for assessing potential environmental exposure to toxic elements. International Journal of Environmental Analytical Chemistry. 2015
17. Van Grieken, R.; Markowicz, A. Handbook of X-ray Spectrometry: Methods and Techniques. New York: Marcel Dekker; 1992.
18. Margui, E.; Van Grieken, R. X-Ray Fluorescence Spectrometry and Related Techniques. New York: Momentum Press; 2013.
19. Gutknecht W, Flanagan J, McWilliams A, Jayanty RKM, Kellogg R, Rice J, Duda P, Sarver RH. Harmonization of uncertainties of x-ray fluorescence data for PM 2.5 air filter analysis. Journal of the Air and Waste Management Association. 2010; 60:184–194. [PubMed: 20222531]

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20. International Organization for Standardization. Geneva, Switzerland: 2008. Evaluation of measurement data - Guide to the expression of uncertainty in measurement.
21. Thompson, M.; Ellison, SLR.; Wood, R. Pure Applied Chemistry. 2002. Harmonized Guidelines for Single-laboratory Validation of Methods of Analysis (IUPAC Technical Report); p. 835-855.
22. Mahmood ZA, Zoha SMS, Usmanghani K, Hasan MM, Ali O, Jahan S, Saeed A, Zaihd R, Zubair M. Kohl (surma): Retrospect and prospect. Pakistan Journal of Pharmaceutical Sciences. 2009; 22:107–122. [PubMed: 19168431]
23. Todd AC. L-shell x-ray fluorescece measurements of lead in bone: theoretical considerations. Physicis in Medicine and Biology. 2002; 47:491–505.

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Highlights

- A portable x-ray fluorescence analyzer is assessed for use in public health.
- Improved detection limits possible using a new optic-enabled technology.
- Analysis of consumer goods and cultural products for toxic metals/metalloids.
- Seven certified reference materials are used to validate accuracy and precision.
- Results from archived samples compare well to atomic emission spectrometry.

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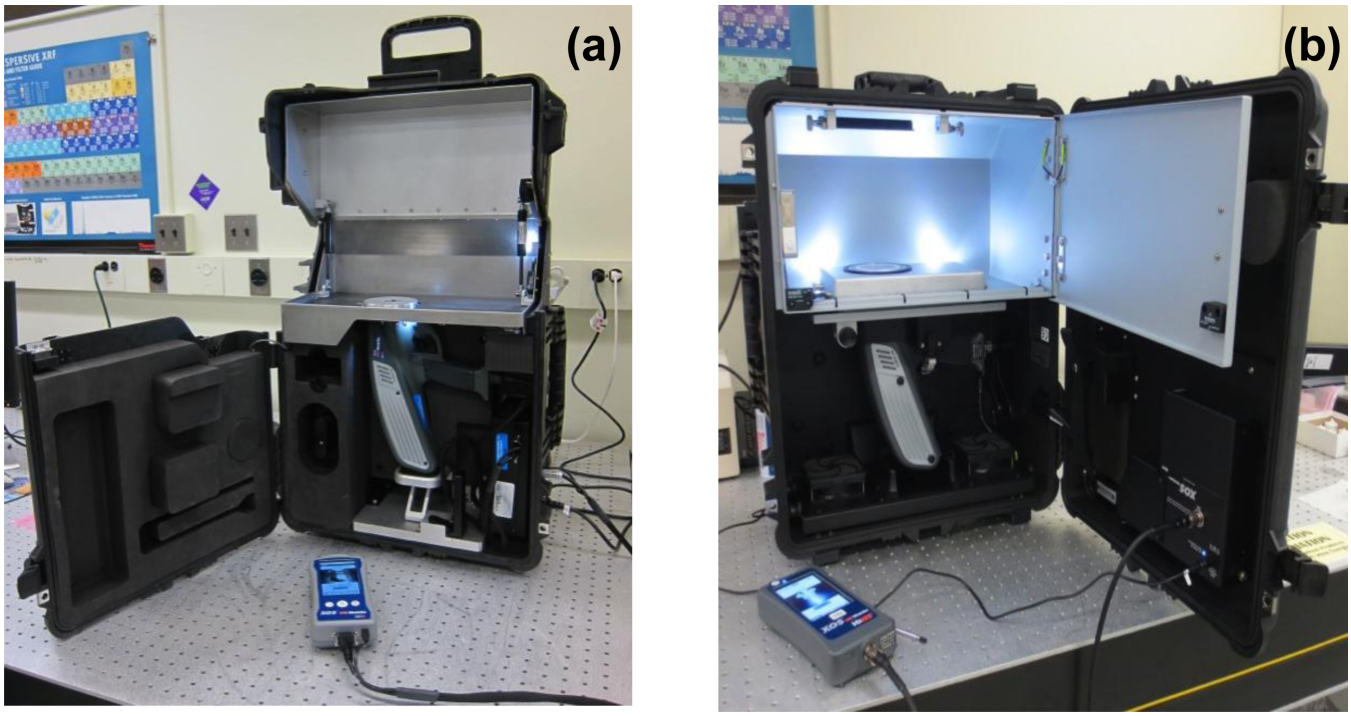

Fig. 1.
(a) Pre-production and (b) final production HD Mobile® instruments.

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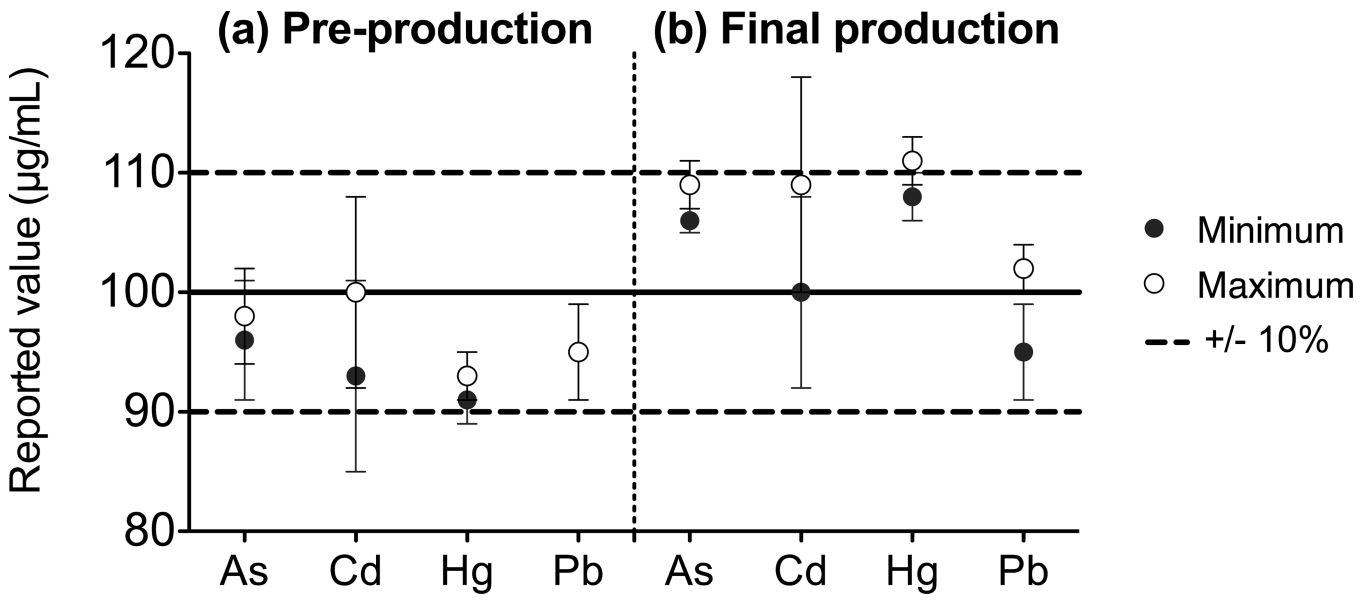

Fig. 2.

Summary of performance data for 100 µg/mL aqueous standards of As, Cd, Hg and Pb, showing the range (minimum and maximum) of mean values (irrespective of sample volume) reported by the HD Mobile® software for (a) pre-production and (b) final production models. Error bars represent the XRF measurement uncertainty as defined in Equation 1.

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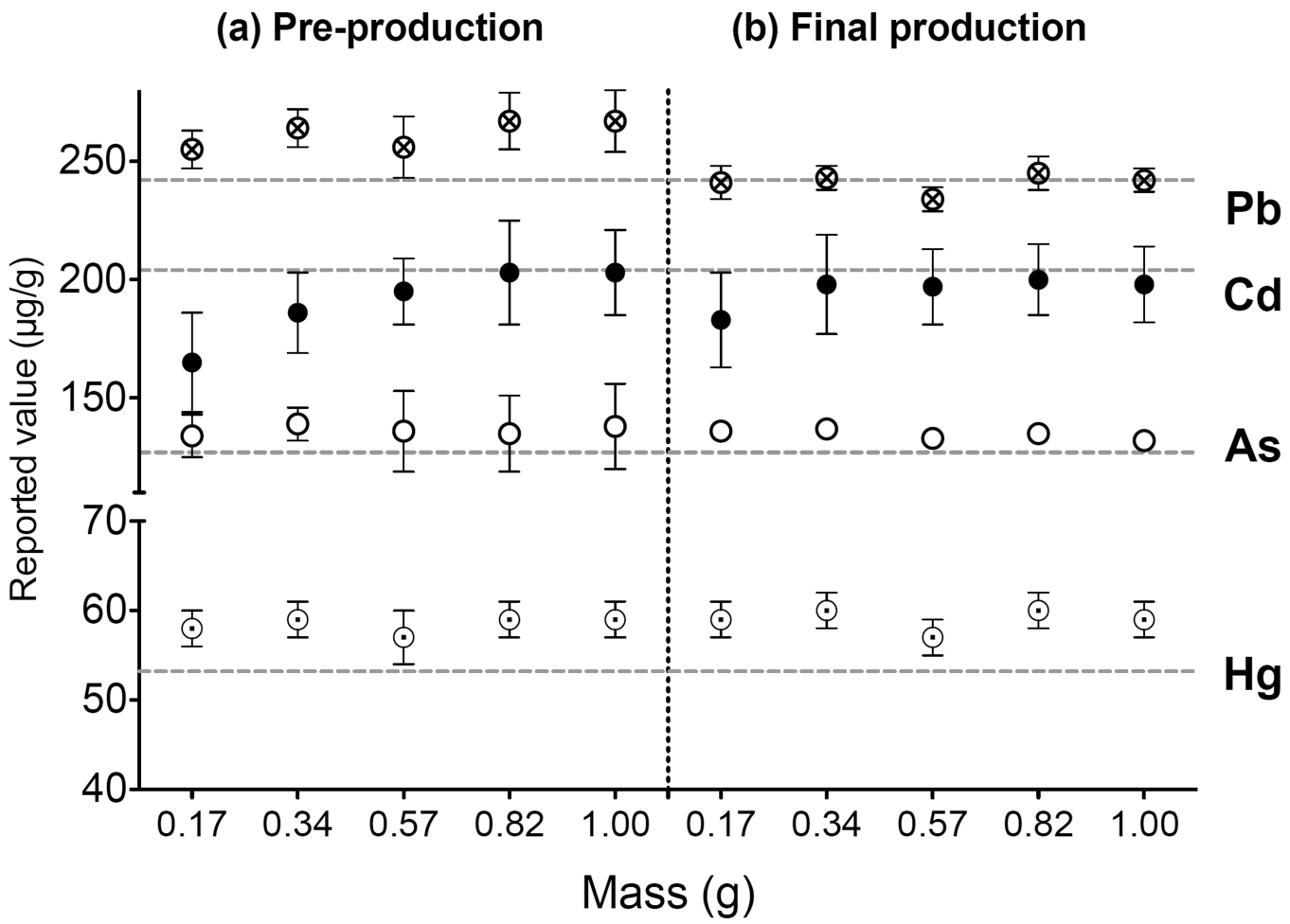

Fig. 3.

Optimization of mass in the sample cup for (a) pre-production and (b) final production HD Mobile® models with IAEA-413 Algae. The dashed lines represent the expected values.

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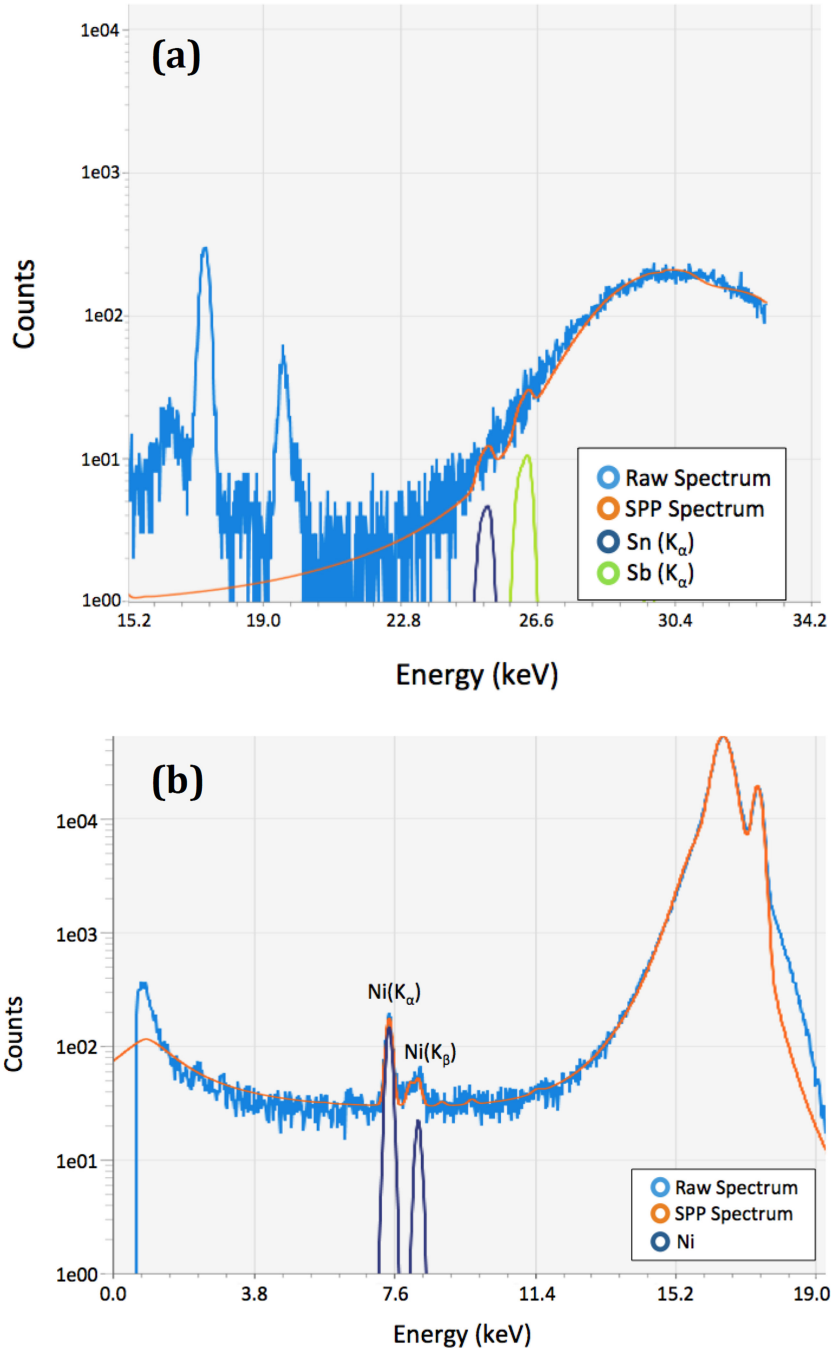

Fig. 4.

Analysis of a boric acid blank sample showing (a) a poor fit (SPP) to the raw high energy spectrum with incorrect detection of Sn and Sb in the pre-production instrument, and (b) internal Ni contamination within the pre-production instrument resulting in Ni peaks appearing in the raw medium energy spectrum. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

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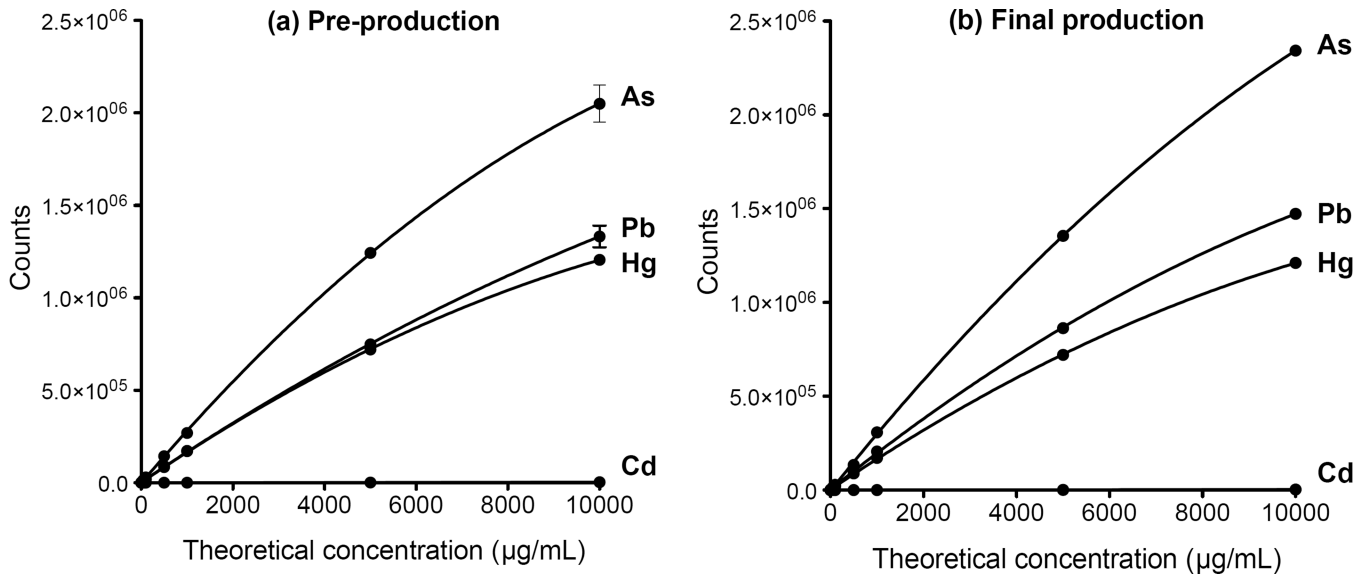

Fig. 5.

HD Mobile® (a) pre-production and (b) final production model As, Cd, Hg, and Pb sensitivity shown as instrument counts with increasing concentration of liquid standards.

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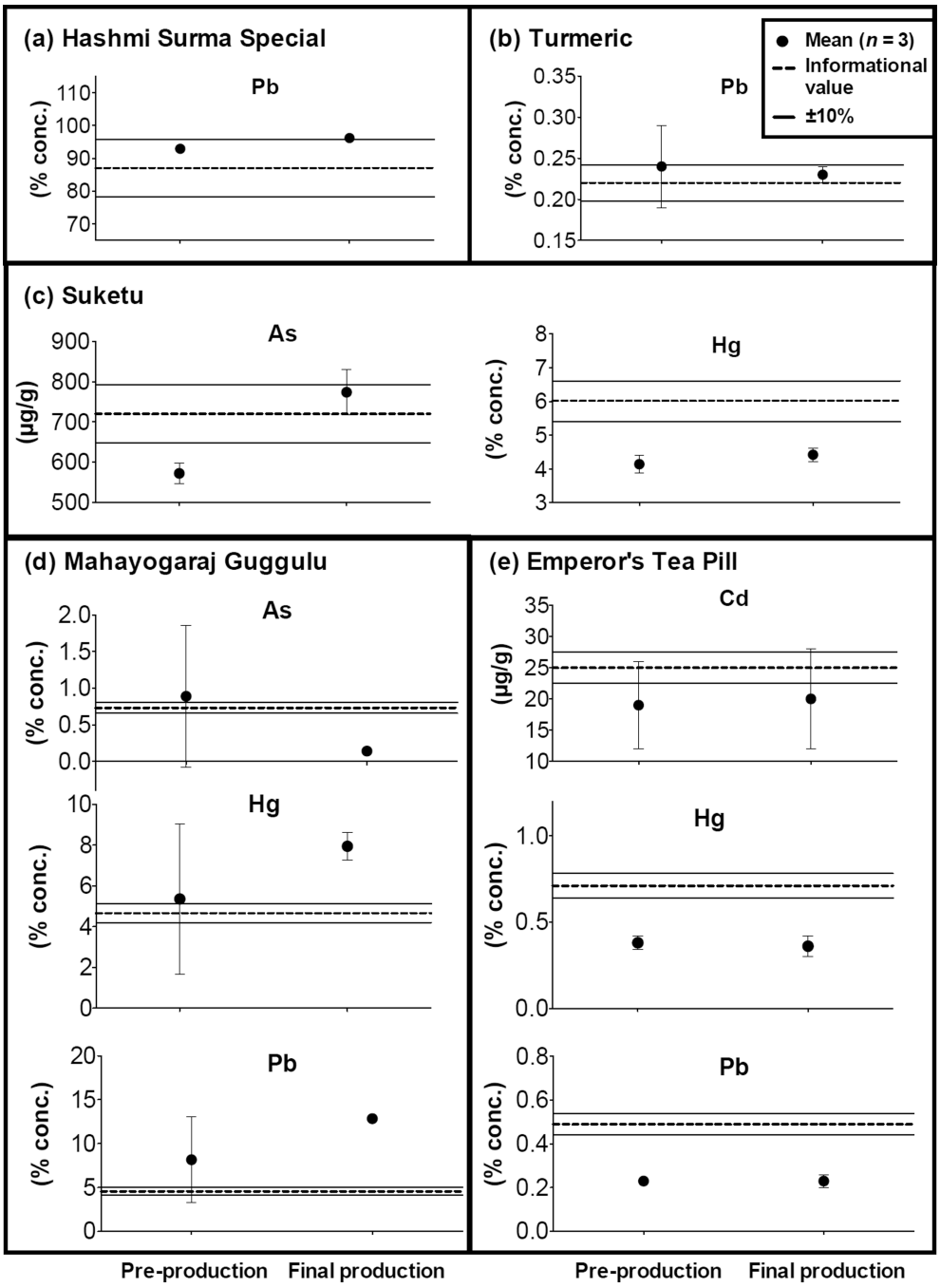

Fig. 6.

HD Mobile® XRF analysis of archived samples of cultural medicines, spices, and personal care products for Pb, Cd, Hg and As compared to the informational value. Error bars where shown indicate the uncertainty as defined in Equation 2.

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Table 1

Linearity of HD Mobile® pre-production and final production models with single element and multi-element solutions

	Pre-production		Final production	
Element	**Slope**	**R^2**	**Slope**	**R^2**
(a) Single element solutions (0 -10,000 µg/mL)				
As	1.00 ×	0.999	**1.03 ×**	1.000
Cd	1.05 ×	1.000	**1.06 ×**	1.000
Hg	**1.12 ×**	1.000	**1.11 ×**	1.000
Pb	**1.02 ×**	0.999	1.05 ×	1.000
(b) Multi-element solutions (0 -2,000 µg/mL)				
As	1.00 ×	0.996	**0.92 ×**	0.984
Cd	1.10 ×	0.999	**1.10 ×**	1.000
Hg	**0.99 ×**	0.998	**1.05 ×**	1.000
Pb	**0.93 ×**	0.997	1.07 ×	1.000

Bold: indicates where the 95% confidence intervals for the single and multi-element slopes do not overlap, i.e., they are different.

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Table 2

LOD in µg/mL for HD Mobile® pre-production and final production instrument calculated according to IUPAC rules and XRF conventional practices with a 10 µg/mL multi-elemental solution

Element	Pre-production LOD (µg/mL)	Final production LOD (µg/mL)		
	IUPAC	XRF	IUPAC	XRF
Cr	4	3	4	4
Mn	2	3	2	3
Fe	2	2	2	2
Co	1	3	2	2
Ni	2	1	2	1
Cu	1	1	1	2
Zn	1	1	1	1
As	1	2	1	1
Se	1	1	1	1
Sr	2	1	1	1
Cd	5	3	4	6
Sn	14	7	15	5
Sb	12	8	33*	14*
Pb	1	1	1	1
Hg	2	4	1	3

*Calculated using a 50 µg/mL multi-elemental solution

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Table 3

LOD in µg/g for HD Mobile® pre-production and final production instrument calculated according to IUPAC rules and XRF conventional practices using solid reference materials.

			Pre-production LOD (µg/g)		Final production LOD (µg/g)	
Element	**Certified Reference Material**	**Certified value (µg/g)**	**IUPAC**	**XRF**	**IUPAC**	**XRF**
Cr	Dogfish Muscle NRC DORM-2	34.7	8	5	7	4
Mn	Lobster Hepatopancreas NRC TORT-2	13.6	2	4	2	5
Fe	Lobster Hepatopancreas NRC TORT-2	105	7	4	6	3
Ni	Algae IAEA 413	113	8	4	9	3
Cu	Orchard Leaves NIST SRM 1571	12	1	2	1	1
Zn	Orchard Leaves NIST SRM 1571	25	2	1	2	1
As	Tuna IRMM BCR-627	4.8	1	1	1	1
Se	Dogfish Muscle NRC DORM-2	1.4	1	1	1	1
Sr	Orchard Leaves NIST SRM 1571	37	5	2	2	2
Cd	Lobster Hepatopancreas NRC TORT-2	26.7	9	9	11	10
Pb	Mussel Tissue NIST SRM 2976	1.19	1	1	1	1
Hg	Dogfish Muscle NRC DORM-2	4.64	1	2	1	1

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Table 4

HD Mobile® performance for pre- and final production models NW and PW ELAP PT samples.

			Pre-production	Final production					
Element	**Target value (µg/mL)**	**Acceptable range (µg/mL)**	**Measured value ± *u* (µg/mL)**	***u* (%)**	**Bias (%)**	**Measured value ± *u* (µg/mL)**	***u* (%)**	**Bias (%)**	**Difference (%)†**
(a) NW Metals									
Al	249.0	223.5 – 274.5	<LOD	--	--	<LOD	--	--	--
V	40.4	37.4 – 43.4	<LOD	--	--	<LOD	--	--	--
Cr	50.0	46.1 – 53.9	42 ± 6	14	−16	51 ± 5	10	2	−18
Mn	146.6	137.3 – 155.9	122 ± 6*	5	−17	134 ± 6	4	−9	−9
Fe	271.4	252.5 – 290.9	226 ± 7*	3	−17	260 ± 7	3	−4	−13
Co	31.56	29.3 – 33.8	27 ± 2*	7	−14	27 ± 3	11	−14	0
Ni	238	223.9 – 252.1	197 ± 3*	2	−17	224 ± 4	2	−6	−12
Cu	34.92	32.8 – 37.1	28 ± 1*	4	−20	32 ± 1	3	−8	−13
Zn	149.8	137.2 – 162.4	135 ± 2*	1	−10	141 ± 2	1	−6	−4
As	36.94	33.2 – 40.7	34 ± 1	3	−8	37 ± 1	3	0	−8
Se	27.28	23 – 31	26.2 ± 0.7	3	−4	26.0 ± 0.8	3	−5	1
Ag	25.72	23.47 – 27.97	26 ± 4	15	1	28 ± 5	18	9	−7
Cd	22.8	21.0 – 24.6	23 ± 4	17	1	21 ± 4	19	−8	10
Sb	22.48	18.9 – 26.0	64 ± 11*	17	185	14 ±10	71	−38	357
Ba	117.6	110 – 125	<LOD	--	--	<LOD	--	--	--
Sr	22.42	20.6 – 24.3	24 ± 1	5	6	27 ± 1*	3	22	−15
Tl	49.02	43 – 55	ND	--	--	ND	--	--	--
Pb	41.24	38 – 45	43 ± 2	5	4	41	5	−1	5
(b) PW Metals									
Al	26.9	23.3 – 30.5	<LOD	--	--	<LOD	--	--	--

				Pre-production	Final production				
Element	Target value (µg/mL)	Acceptable range (µg/mL)	Measured value ± *u* (µg/mL)	*u* (%)	Bias (%)	Measured value ± *u* (µg/mL)	*u* (%)	Bias (%)	Difference (%)[†]
V	41.3	37.4 – 45.2	<LOD	--	--	<LOD	--	--	--
Cr	11.0	10.1 – 11.9	6 ± 4[*]	67	−45	14 ± 3	21	27	−57
Mn	61.7	56.0 – 67.4	52 ± 4	8	−16	56 ± 5	9	−9	−7
Fe	22.0	19.3 – 24.7	14 ± 2[*]	14	−36	16 ± 2[*]	13	−27	−13
Ni	16.9	15.4 – 18.4	13.0 ± 0.7[*]	5	−23	12.1 ± 0.9[*]	7	−28	7
Cu	186	174 – 198	169 ± 4[*]	2	−9	175 ± 3	2	−6	−3
Zn	151	136 – 166	145 ± 3	2	−4	148 ± 3	2	−2	−2
As	1.66	1.39 – 1.93	1.4 ± 0.3	21	−16	1.5 ± 0.1	7	−10	−7
Se	4.68	4.14 – 5.22	4.6 ± 0.3	7	−2	4.6 ± 0.4	9	−2	0
Mo	1.54	1.42 – 1.66	ND	--	--	ND	--	--	--
Ag	28.3	23.2 – 33.4	28 ± 4	14	−1	32 ± 5	16	13	−13
Cd	2.71	2.38 – 3.04	3 ± 2	67	11	<LOD	--	--	--
Sb	3.08	2.51 – 3.65	37 ± 9[*]	24	110	<LOD	--	--	--
					1				
Ba	128	116 – 140	<LOD	--	--	<LOD	--	--	--
Hg	0.594	0.486 – 0.702	<LOD	--	--	<LOD	--	--	--
Tl	0.805	0.658 – 0.952	ND	--	--	ND	--	--	--
Pb	0.954	0.774 – 1.13	<LOD	--	--	0.9 ± 0.7	78	−6	--
U	2.96	2.69 – 3.23	ND	--	--	ND	--	--	--

[*] result outside of the acceptable range, i.e., ELAP quality specifications (±3SD for NW and ±2SD for PW)

[†]% Relative difference between the pre- and final production instruments

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Table 5

HD Mobile® XRF analysis of various biological CRMs

			Pre-production			Final Production			
Sample matrix	**Element**	**Assigned value* ± *U* (µg/g)**	**Measured value ±*u* (µg/g)**	***u* (%)**	**Bias (%)**	**Measured value ± *u* (µg/g)**	***u* (%)**	**Bias (%)**	**Difference (%)†**
Algae IAEA 413	K	10740 ± 270	8000 ± 1000	13	**−26**	10500 ± 700	7	−2	−24
	Ca	3143 ± 112	2600 ± 200	8	**−17**	2900 ± 200	7	−8	−10
	Cr	377 ± 14	380 ± 20	5	1	370 ± 20	5	−2	3
	Mn	158 ± 3.4	150 ± 8	5	−5	170 ± 20	12	8	−12
	Fe	1370 ± 39	1310 ± 40	3	−4	1380 ± 70	5	1	−5
	Ni	113 ± 4.9	101 ± 5	5	−11	106 ± 7	7	−6	−5
	Cu	11.1 ± 0.5*	8 ± 1	13	**−28**	10 ± 1	10	−10	−20
	Zn	169 ± 3.3	169 ± 6	4	0	169 ± 7	4	0	0
	As	127 ± 6.6	140 ± 20	14	10	133 ± 6	5	5	5
	Cd	204 ± 8.5	190 ± 20	11	−7	200 ± 20	10	−2	−5
	Hg	53.2 ± 4*	59 ± 3	5	11	60 ± 2	3	13	−2
	Pb	242 ± 7	260 ± 10	4	7	242 ± 7	3	0	7
	Cl	690*	--	--	--	700 ± 300	43	1	--
Orchard Leaves NIST SRM 1571	K	14700 ± 300	12000 ± 2000	17	**−18**	14000 ± 1000	7	−5	−14
	Ca	20900 ± 300	19000 ± 2000	11	−9	18000 ± 1000	6	−14	6
	Mn	91 ± 4	110 ± 10	9	**21**	90 ± 20	22	−1	22
	Fe	300 ± 20	260 ± 20	8	−13	270 ± 20	7	−10	−4
	Cu	12 ± 1	8 ± 1	13	**−33**	10 ± 2	20	**−17**	−20
	Zn	25 ± 3	26 ± 3	12	4	25 ± 3	12	0	4
	As	10 ± 2	11 ± 2	18	10	10 ± 2	20	0	10
	Br	10*	10 ± 1	10	0	9 ± 1	11	−10	11
	Rb	12 ± 1	13 ± 1	8	8	12 ± 1	8	0	8
	Sr	37 ± 1	39 ± 3	8	5	40 ± 3	8	8	−3
	Pb	45 ± 3	45 ± 3	7	0	44 ± 5	11	−2	2

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			Pre-production			Final Production			
Sample matrix	**Element**	**Assigned value* ± *U* (µg/g)**	**Measured value ±*u* (µg/g)**	***u* (%)**	**Bias (%)**	**Measured value ± *u* (µg/g)**	***u* (%)**	**Bias (%)**	**Difference (%)†**
Mussel Tissue NIST SRM 2976	S	19000*	11000 ± 2000	18	**−42**	13000 ± 2000	15	**−32**	−15
	Cl	57000 ± 5000	47000 ± 5000	11	**−18**	48000 ± 6000	13	**−16**	−2
	K	9700 ± 500	7400 ± 800	11	**−24**	8000 ± 1000	13	**−18**	−8
	Ca	7600 ± 300	5800 ± 500	9	**−24**	6000 ± 1000	17	**−21**	−3
	Mn	33 ± 2	31 ± 5	16	−6	31 ± 6	19	−6	0
	Fe	171 ± 4.9	140 ± 10	7	−18	142 ± 9	6	−17	−1
	Zn	137 ± 13	140 ± 20	14	2	124 ± 6	5	−9	13
	As	13.3 ± 1.8	12 ± 1	8	−10	14 ± 1	7	5	−14
	Se	1.80 ± 0.15	1.3 ± 0.5	38	−28	1 ± 1	100	−44	30
	Br	329 ± 15	290 ± 20	7	−12	258 ± 7	3	**−22**	12
	Rb	4.14 ± 0.09	6 ± 1	18	**52**	3 ± 1	33	**−28**	109
	Sr	93 ± 2	80 ± 10	12	−13	74 ± 2	3	**−20**	9
	Pb	1.19 ± 0.18	2 ± 2	79	**61**	2 ± 1	50	**68**	−4
Lobster Hepato-pancreas NRC TORT-2	Mn	13.6 ± 1.2	12 ± 4	37	−13	13 ± 4	31	−4	−9
	Fe	105 ± 13	90 ± 20	23	−14	98 ± 7	7	−7	−8
	Cu	106 ± 10	100 ± 20	20	−6	105 ± 5	5	−1	−5 0
	Zn	180 ± 6	190 ± 30	16	6	190 ± 6	3	6	0
	As	21.6 ± 1.8	21 ± 3	15	−3	25 ± 1	4	**16**	−17
	Se	5.63 ± 0.67	6 ± 1	14	8	6 ± 1	17	**7**	1
	Sr	45.2 ± 1.9	44 ± 8	19	−2	43 ± 2	5	**−5**	3
	Cd	26.7 ± 0.6	27 ± 7	27	3	23 ± 7	30	−14	19
	Cr	34.7 ± 5.5	26 ± 6	24	**−25**	33 ± 7	21	**−5**	−21
Dogfish Muscle NRC DORM-2	Fe	142 ± 10	110 ± 20	18	**−23**	130 ± 20	15	−8	−15
	Zn	25.6 ± 2.3	25 ± 2	10	−2	26 ± 6	23	2	−3
	As	18.0 ± 1.1	18 ± 1	8	0	20 ± 1	5	11	−10
	Se	1.4 ± 0.09	1.3 ± 0.4	28	−4	1.5 ± 0.4	27	7	−11
	Hg	4.64 ± 0.26	4 ± 1	19	−5	5 ± 1	20	8	−12
Tuna Fish IRMM BCR-627	As	4.8 ± 0.3	4 ± 1	16	−9	5.4 ± 0.4	7	13	−19

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Sample matrix	Element	Assigned value* ± *U* (μg/g)	Pre-production			Final Production			Difference (%)†
			Measured value ±*u* (μg/g)	*u* (%)	Bias (%)	Measured value ± *u* (μg/g)	*u* (%)	Bias (%)	
Tuna Fish IRMM ERM-CE464	Hg	5.24 ± 0.10	5 ± 1	12	−4	5.3 ± 0.6	11	1	−5

* indicates reference (±U) or informational values (no U) from the CRM certificate of analysis

† % relative difference between the pre- and final production instruments

Bolded values represent > |15%| bias relative to the certified value