Evaluation of a new optic-enabled portable X-ray fluorescence spectrometry instrument for measuring toxic metals/metalloids in consumer goods and cultural products☆

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ARTICLE INFO

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 make 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 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.

1. 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 an 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

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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 (ICP-OES), which require time-consuming sample preparation procedures. XRF's simplicity, non-destructive analyses and its lower cost (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 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 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.

2. Experimental

2.1. 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 enhance 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, improving elemental detection limits and shortening 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 min.

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 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,