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Benchtop x-ray fluorescence to quantify elemental content in nails non-destructively

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Abstract

Metals continue to impose health issues among world populations. A non-invasive alternative biomarker for assessment of metals and other elements has been explored in other studies using toenail samples. Some benefits of using toenails as biomarkers over blood samples include cost efficiency, ease of collection, and a longer biological half-life within samples. The objective of this study was to employ desktop XRF for the purpose of measuring metal concentrations in human nail samples, thus conducting a non-destructive assessment. These benefits paired with comparable accuracy in exposure detection could prove toenail samples to be a preferred biomarker for many studies. Current elemental quantification techniques in toenail samples could be improved. The standard practice for measuring metal exposure in toenails, inductively coupled plasma mass spectrometry (ICP-MS), has a counterpart in x-ray fluorescence. While maintaining similar quantification capabilities, x-ray fluorescence could provide decreased cost, preservation of samples, and ease of operation. Portable XRF machines have been tested for measuring toenail samples, but they have drastically increased detection limits in comparison to ICP-MS. New benchtop XRF systems should give comparable detection limits to ICP-MS. This study compares the benchtop XRF measurements of lead (Pb), copper (Cu), iron (Fe), and Selenium (Se) levels to that of ICP-MS measurements of toenail samples and calculates estimated detection limits for 23 other elements. We found strong correlations for the toenail lead (R^2=0.92), copper (R^2=0.95), selenium (R^2=0.60), and iron (R^2=0.77) comparison between desktop XRF and ICP-MS measurements. Median minimum detection limits over the 23 elements were found to be 0.2 μg/g using a 7.5-minute measurement. Benchtop XRF provides a lower detection limit than previously studied portable XRF machines, which gives it the capability of accurately detecting

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Author Contributions Statement

Aaron J Specht: Conceptualization, Methodology, Investigation, Writing, Visualization

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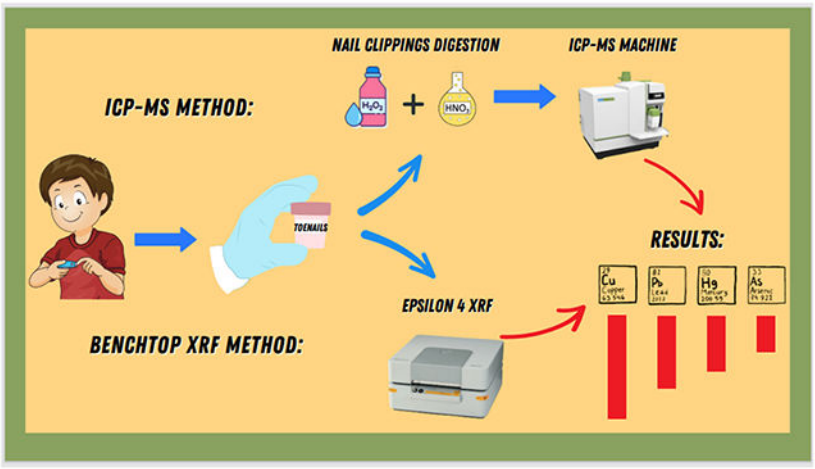
Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

almost any desired element in nail samples. Benchtop XRF provides a non-destructive alternative to ICP-MS in surveillance of nail samples.

Graphical Abstract



1. Introduction

Heavy metal toxicity continues to be an ongoing, worldwide issue with deleterious health effects recorded at even the lowest exposures.(1-6) The most common approach for assessing heavy metal body burdens is measuring concentrations in blood, which is used as a standard in many clinical settings. However, metal measurement in blood is invasive, requires trained phlebotomists and advanced chemical analysis equipment to perform accurate analyses, and is costly.(7-9) More accessible methods for assessing metal body burden could facilitate research into metal-related health issues, especially for those communities most impacted by such exposure. Recently, studies have adopted nails as a potential biomarker of exposure to many metals.(7,10,11)

A primary route of accumulation in nails relates to sulfide bonds within the tissue. However, other routes of accumulation exist as metals like lead do not bind within the nail under this mechanism. Either route of accumulation in nail typically result in an integrated assessment of exposure over months to a year and will reflect exposure from a period of approximately 6-12 months prior to toenail clipping.(7,12,13) Other work has also suggested that toenails reasonably reflect heavy metal exposure over even longer periods of time,(13) although this is likely because lifestyle behaviors tend to be consistent over time.(14) However, while much easier to collect, typical analysis of toenail metals using inductively coupled plasma mass spectrometry (ICP-MS) can be expensive. In this study, we utilize the cheaper, more efficient, and more accessible XRF, which serves as an alternative to measuring nail heavy metals with the same detection standards utilized for ICP-MS.

X-ray fluorescence (XRF) is a useful technology for measuring metal concentrations in human samples because of its lower cost compared to ICP-MS, and relative ease of operation compared to other technologies. Additionally, as opposed to ICP-MS, XRF is

a non-destructive method, meaning that valuable biological samples can be used multiple times rather than being used for a single analysis. XRF uses an x-ray source to excite atoms in a sample, which will then produce signals specific to the element of the original excited atom. These characteristic x-rays can then be collected to quantify the concentration of each element in a given sample. Newer benchtop XRF systems allow for a more powerful measurement approach than previously used portable or handheld XRF measurements.(15-17) Furthermore, preliminary investigations of blood spots with these devices have identified detection limits suitable for determining blood metal levels.(18) Thus, the device should be well-suited to measure nails with similar detection efficiencies that have been expected from the gold standard ICP-MS measures in the past. In this study, we measured nails using a benchtop XRF system and compared the results to those from ICP-MS.

2. Methods

a. Nail Collections and Processing

The nails used for this comparison were collected as part of the Normative Aging Study, a longitudinal cohort of men from the Greater Boston, Massachusetts area.(19) The toenail clippings were collected in the early 2000s. A rigorous cleaning regimen was utilized to ensure no contamination was present, as is standard in the field, including washing with 1% triton, deionized (DI) water, and acetone. (17,20) The samples were then freeze dried to remove any remaining moisture prior to measurements. We included Pb, Cu, Se, and Fe in the validation measurements. These elements were chosen, as they met a few criteria in order to be able to be used in our validation: 1) the participants had initial values able to be distinguished by both ICP-MS and XRF; 2) the range of those values had enough variation to allow us to determine high versus low values from participants; and, finally, 3) these elements encompass a range of energies from 6 keV to 12 keV for characteristic x-ray signals from XRF. This range would include most elements measured in previous studies of toxic and nutritional elements measured in nails. We used 30 individuals nail samples total, with 10 samples being only analyzed for Pb. Thus, Pb the total was 30, whereas for Fe, Cu, and Se the total individuals included was 20. None of these samples had nail polish applied prior to sampling.

b. Benchtop X-ray Fluorescence Methodology

The benchtop x-ray fluorescence equipment utilized in this study was the Epsilon 4 (Malvern Panalytical, Marlborough, MA). The Epsilon 4 utilizes a 15-watt x-ray tube with 50 kV max tube voltage. As is done routinely with XRF analysis, the Epsilon 4 software has standard deconvolution protocols that use a series of gaussians along with a polynomial background to identify net counts associated with each element of interest.(21-24) The samples were placed in the center of a 30 mm XRF cup and covered with a 4 micrometer thin polypropylene film. Importantly, for XRF analysis the nails do not need to be homogenized or digested.(15,17) Thus, the preparation after cleaning is eliminated using this method. For our heavy metal measurements, we utilized the full energy beam at 50 kV and 300 μA and collected data for 7.5-minutes for each nail sample.

As has been done in previous studies,(17,21) standard phantoms made using epoxy resin and sodium chloride to have similar properties to toenails are doped with known concentrations of metals of interest in order to appropriately calibrate the machine for elemental quantification in toenails.(25) As reported in previous studies, phantoms are made of varying thicknesses similar to those of the human toenail.(13) Subsequently, samples are measured and the strength of characteristic spectra peaks for metals of interest are translated into metal concentrations based on the formula derived from calibrating the system with standard phantoms. Successful quantification, therefore, depends on the strength of the machine, precise calibration with phantom samples, and a valid normalization approach. Previous research using a less powerful instrument has validated the use of phantom samples and the normalization approach utilized here.(17,21,22) The normalization approach is based on the Compton scattering peak, which was shown to correct for the mass and thickness variations within nail samples that would otherwise influence the accuracy of the approach.(16,17) For this calibration, results from the benchtop XRF are reported in micrograms per gram of nail material, which is the standard reporting unit from ICP-MS as well.

C. Inductively Coupled Plasma Mass Spectrometry

After measurement with the benchtop XRF, all clippings were digested in 3 mL of trace metal grade nitric acid and 1 mL of hydrogen peroxide at room temperature for 48 hours. Then the samples were diluted with 6 mL of DI water prior to analysis. The analysis was done using an internal standard of scandium, yttrium, and terbium. For further quality control and assessment, we used ERM-DB001, a certified standard for human hair, with varying concentrations of a continuous calibration standard, digestion duplicates, and NIST1643f standard for trace elements in water. In our analysis, there were no metals analyzed that were below the detection limits. In analysis duplicates, the standard error was 6.5% on average for all metals analyzed. In ERM-DB001, the average recovery percentage was found to be 85%. Our calibration standards had an average recovery of 94% for all metals, and the NIST1643f standard had an average of 90%. The elements analyzed in this sample did not show signs of interference through observed changes with the use of internal standards for matrix effects and instrumental reduction with kinetic energy discrimination.

d. Statistical Analysis

Pearson correlations were used to determine the relationship between XRF and ICP-MS measurements. Negative values were included in XRF measurements, as this is a point estimate of the concentration including the error.(26,27) Redefining such measurements could artificially increase correlations because of reduced variance. The minimum detection limits (MDL) are calculated based on the formula

$$MDL = 2 * \frac{\sqrt{BKG}}{m} \quad (1)$$

where BKG is the background counts measured using a 0 ppm toenail phantom for the particular element and m is the slope of the regression between counts and ppm taken from

our nail measurements.(28) Using the real nails to establish the detection limits can account for any potential uncertainty that may be introduced by the natural error in applying the method to human samples, rather than perfectly created lab standards. As an additional determination of the limit of detection, nails underwent 30 repeated measurements using the same X-ray settings, and the MDL was taken as twice the standard deviations of the result from all 30 measurements.

3. Results

a. Elemental Concentrations

Table 1 indicates the average elemental content of Fe, Cu, Se, and Pb measured in nails using both XRF and ICP-MS. The average age at clipping date was 82.8 ± 5.5 years for our participants. The selection of these specific metals for comparison between desktop XRF and ICPMS techniques in toenails is primary based on their biological relevance, potential public health implications, and the capabilities of the analytical techniques. Fe, Cu, Se, and Pb are of public health concerns particularly in very elevated quantities. The nails had a mass of 0.1 ± 0.05 grams. Twenty nails were included in the comparison between Fe, Cu, and Se, but the Pb assessments included an additional 10 (total 30) that were not analyzed for Fe, Cu, and Se. For Fe, 2 samples were below the detection limit for ICP-MS and removed from the validation analysis.

b. Correlations between XRF and ICP-MS and Limit of Detection

Figures 1 below show Pearson correlation plots comparing XRF and ICP-MS. In Table 1, we calculated limits of detection with the XRF approach for each of the metals identified using 30 repeated measurements of human nails identifying the minimum detection limit as twice the standard deviation of the concentration over the 30 measurements.

4. Discussion

This study represents the first to assess benchtop XRF as a method for quantification of elements in nail. Feasibility and validity studies for using XRF to quantify toenail metal concentrations have exclusively used portable XRF technology, largely because it does not require specimen collection and can be used directly in the field.(10,11,15) Original attempts to compare metal concentration measures obtained by portable XRF and ICP-MS, the gold standard for toenail metal quantification, resulted in agreement between the two technologies, but with higher detection limits (Minimum detection limit = 3.2 μg/g for Mn and 0.6 μg/g for Pb).(15,29-32) Nonetheless, the desktop XRF we used here has much more power, which lowered the detection limits drastically (Minimum detection limit = 0.09 μg/g for Mn and 0.1 μg/g for Pb).

Although, the ultra-sensitive nature of ICP-MS is advantageous for quantifying elements at minutest levels, the non-destructive attribute of desktop XRF emerges as a valuable complement. This allows for analysis of concentrations through multiple methods while offering a versatile approach that may be particularly beneficial in situations where sample preservation and subsequent analyses are imperative.

The precision of the portable XRF technology, as with other XRF technology, is limited by the power available to the device.(33) In order to measure biologically relevant concentrations, greater precision is desirable, especially for measuring low, chronic exposure to heavy metals that are likely to influence aging-related disease. As such, desktop XRF can be used when portability is not necessary.(18) The primary difference between portable and desktop XRF is the power output, which directly relates to a reduction in the detection limit of the device. For example, in the case of manganese, the desktop XRF in our study has an estimated power output and detectability improvement of 35 times over a typical portable XRF device.(15,21) While portable XRF may be beneficial for fieldwork and in vivo measurements due to its simplicity and short measurement time, desktop XRF has the potential to detect significantly lower concentrations of metals in biological samples.(18) For many environmental studies, desktop XRF is necessary for its ability to achieve significantly lower minimum detection limits that will allow us to measure the concentrations of even background exposures to many environmental elemental exposures. Nails, for example, primarily have concentrations of approximately 1 ppm or lower. This would make measurements with a handheld XRF difficult for individuals not heavily exposed.(15) However, the benchtop XRF with detection limits of 0.05 ppm would be able to capture most elements that accumulate even with very limited exposure. This study confirmed the utility of desktop XRF for measuring metal concentrations in nail samples, and future studies could confirm this capability for other biologic samples. Toenails are often used as a biomarker of long-term exposure, reflecting the cumulative exposure over an extended period.(10,11) The accumulation of metals in toenails is often as a result of various biological processes and environmental exposures. The biological mechanisms for this pathway includes ingestion diet which is the primary route for metals entering the body, throughput distribution in the body through the bloodstream which are later transported to different organs and tissue including nails, and most importantly through keratinization involving new nail cell birth during which minerals and metals can become part of the nail structure. Although studies have identified cleaning as successfully removing potential contamination or as unnecessary in certain circumstances, there is little literature on how external application of polish may impact the measurements even after removal.(34,35) This may need to be explored further to elucidate potential uses, especially in studies where nail polish is more prevalent. Finally, these measurements were restricted to participants in a study focused on older men. Studies have shown that there are common changes in the nail composition and growth rates for older versus younger individuals, which may need to be taken into account as an important confounder in studies utilizing nails as a biomarker of exposure. However, in our case, since the validation results mainly focus on the concentrations of nails, which did not differ significantly from previous studies in this regard, this point would not bias our results.(36,37)

While all relationships were significant, Se and Fe had more error in the associations between XRF and ICP-MS. Se has a known interference with argon, which is used universally in ICP-MS, so that is likely a significant source of error in the relationship – even after consideration of interference removal using kinetic energy discrimination. Fe the error is more likely to be introduced on the XRF side, but still presents with a very strong relationship. The energies of iron have overlap with Mn, however current approaches

for deconvolution of the spectra typically disentangle these peaks well. It is possible this gives residual error in the relationship. Nonetheless, each of these relationships is still strong enough to identify both ICP-MS and XRF as effectively giving concentration values. Future studies may be able to identify more robust relationships with greater variation in concentrations of elements not included here.

While the desktop XRF is very promising for multi-elemental analysis at low detections, a few limitations from its use may be in terms of the range of the elements it can effectively detect. In addition, since XRF generally depends on the excitation of atoms by X-rays and the emitted fluorescence is used in the elemental content determination, the energy levels may impose some constraints on the detection of certain elements for particularity those with lower atomic numbers or specific X-ray emission energies. The elements validated here do encompass a range of elements from ~6 keV to 12 keV. However, the elements were limited by the amount of variation achievable in samples from 20-30 individuals. With more variation in sample concentrations, or in certain circumstances detectable levels such as with cadmium, we would be able to validate these results across a wide range of elements. However, these results do seem to indicate that reliable analysis can be provided by XRF for many elements.

In summary, the high-powered benchtop XRF used in this study is capable of nail measurements with detection limits on the order of 0.05 ppm – a detection limit that can be optimized based on the elements of interest in a sample. This should be able to capture almost all heavy metals, nutritional elements, and many other trace elements in human nail. Human nail serves as an easy to collect biomarker. With the advent of XRF technology accurately mimicking ICP-MS, nail measurements are made much easier with incredibly limited preparation time in comparison to alternative biomarkers for environmental exposures.

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Highlights

- Benchtop x-ray fluorescence can be used to effectively and non-destructively measure elements in nails in minutes
- Nail are a good biomarker for environmental exposure and nutrition with easy, non-invasive collection procedures.
- Benchtop x-ray fluorescence achieved detection limits on par with inductively-coupled plasma mass spectrometry for these environmental measurements with an average detection limits of 0.2 ug/g in nail over all elements.

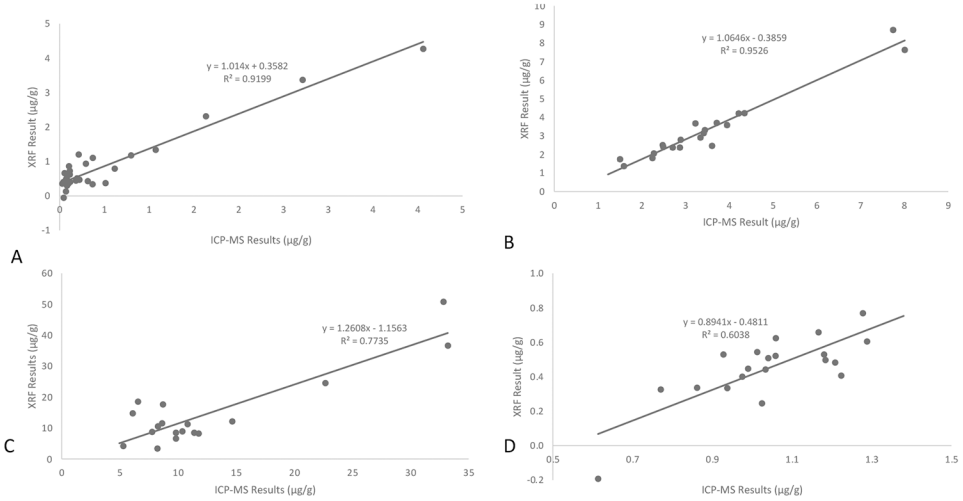

Figure 1.

XRF versus ICP-MS values A) for nail Pb measurements (n=30); B) for nail Cu measurements (n=20); C) for nail Fe measurements (n=18); and D) for nail Se measurements (n=20).

Table 1.

Elemental concentrations from XRF and ICP-MS.

XRF (μg/g)	Median	25th Percentile	75th Percentile
Fe	10.9	8.5	16.9
Cu	5.7	4.7	7.4
Se	0.49	0.38	0.53
Pb	0.57	0.42	0.98
ICP-MS (μg/g)	**Median**	**25th Percentile**	**75th Percentile**
Fe	9.3	7.5	11.5
Cu	3.3	2.5	3.8
Se	1.0	0.97	1.2
Pb	0.20	0.10	0.40

Table 2.

Minimum detection limits (μg/g), average concentration of 30 repeated measures of one sample, and coefficient of variation percentage for 23 elements using benchtop XRF calculated using 30 repeated measurements of nails.

Element	Minimum Detection Limit (μg/g)	Concentration (μg/g)	Coefficient of Variation %
Na	11.84	400.38	1.48
Mg	2.54	126.00	1.01
Al	26.72	105.00	12.72
Si	0.57	1.68	16.96
P	0.23	0.98	11.73
S	1.03	293.50	0.18
Cl	1.51	4.54	16.63
Ca	0.24	570.00	3.60
Ti	0.25	1.19	10.50
V	0.02	0.03	31.25
Cr	0.50	0.60	39.97
Mn	0.09	1.21	3.73
Fe	0.50	14.83	1.69
Co	0.01	0.04	11.90
Ni	0.06	0.36	8.24
Cu	0.12	10.08	0.60
Zn	0.18	85.32	0.11
As	0.002	0.06	1.67
Se	0.06	0.78	3.83
Br	0.24	2.21	5.42
Hg	1.26	2.37	26.58
Pb	0.13	1.30	5.00
Cd	0.01	0.03	16.67