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Portable XRF as a rapid determination tool to detect ppm levels of Ni, Zn, As, Se and Pb in human toenails: A South India case study

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Abstract

Chronic exposure to inorganic pollutants adversely affects human health. Inductively coupled plasma mass spectrometry (ICP-MS) is the most common method used for trace metal(loid)s analysis of human biomarkers. However, it leads to sample destruction, generation of secondary waste and significant recurring costs. Portable x-ray fluorescence (XRF) instruments can rapidly and non-destructively determine low concentrations of metal(loid)s. In this work, we evaluated the applicability of portable XRF as a rapid method for analyzing trace metal(loid)s in toenail samples from three populations ($n = 97$) near the city of Chennai, India. A Passing Bablok regression analysis of results from both methods revealed there was no proportional bias among the two methods for nickel (measurement range ~ 25 to 420 mg/kg), zinc (10 to 890 mg/kg) and lead (0.29 to 4.47 mg/kg). There was a small absolute bias between the two methods. There was a strong proportional bias (slope = 0.253, 95% CI: 0.027, 0.614) between the two methods for arsenic (below detection to 3.8 mg/kg), and for selenium when the concentrations were lower than 2 mg/kg. Limits of agreement between the two methods using Bland-Altman analysis were derived for nickel, zinc and lead. Overall, a suitably calibrated and evaluated portable XRF shows promise in making high throughput assessments at population scales.

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⁴Supporting Information

Supporting information is included showing an example spectra from the XRF, demographic variables from the population, distribution comparisons by method, tables of summary data by site, detailed correlation results, detailed statistical test results, bablok regression results, and box-plots by site.

Keywords

Portable XRF; ICP-MS; toenails; high correlation

1. Introduction

Industrial pollution has increased contamination of the environment by toxic heavy metals^{1,2}. Exposure pathways for inorganic pollutants include inhalation³, dermal and dietary uptake¹. Chronic exposure to heavy metals has been associated with neurodevelopmental, hormonal, reproductive and gastrointestinal health effects in humans^{4,5}. Here we evaluate a method for rapid detection of multiple heavy metals and metalloids in human nails that can facilitate population-wide assessments in remote regions and countries, with minimal experimental costs.

Blood, urine, hair and nails are the most commonly used biomarkers for studying human metal(loid) exposure. Several studies have reported the utility of using toenails as a preferred biomarker⁶⁻⁸. Toenails provide a long-term integrated record of exposure (2-12 months) and can be collected non-invasively, leading to greater acceptability by volunteers⁹⁻¹¹. Nails also often have higher concentrations of metal(loid)s compared to body fluids and tissues and can therefore be detected more easily¹². Toenails are less prone to exogenous contamination like bleaching, dyeing and other cosmetic exposures that could potentially influence elemental exposure assessment^{6,7}.

Metal(loid)s are conventionally quantified by inductively coupled plasma mass spectrometry (ICP-MS). ICP-MS is a robust and sensitive method but has a few limitations. Samples must be transported back to a laboratory, and require acid digestion which leads to sample destruction and production of secondary hazardous waste. The instrument requires meticulous operation to avoid contamination and issues with drift and interferences in order to obtain accurate and precise concentration results.

By contrast, portable x-ray fluorescence (XRF) instruments are mobile, do not require sample processing and are non-destructive. They have potential to provide time-efficient, high-throughput and cost-effective measurements^{13,14}. In recent years, XRF has been extensively used as a rapid screening tool in geological explorations, locating hotspots of contamination, and for analysis of biological samples¹⁵⁻¹⁹.

XRF has been shown to accurately determine concentrations of heavy metals and metalloids in model human nails/phantom nails, made of polyester or other commercial resins and solidifying agents dosed with known quantities of metal(loid)s, for zinc, selenium, arsenic, mercury and chromium²⁰⁻²⁴. Validation with real nail clippings and comparison with ICP-MS has been performed for manganese and lead¹⁷. Results show a high correlation coefficient for manganese ($r = 0.91$) but a much lower value for lead ($r = 0.3$). This may have occurred because most of the sample concentrations were below the detection limit of the XRF for Pb (0.6 mg/kg).

The goal of this work was to evaluate the usability of XRF, in particular portable XRF, for reliably measuring multiple elements from human nails. We evaluated the capability of portable XRF to reliably quantify multiple elements (nickel, zinc, arsenic, selenium and lead) in toenail samples, by assessing the concentrations of these elements in ninety-seven toenail samples determined by both portable XRF and ICP-MS.

2. Material and Methods

2.1. Toenail sample collection and preparation

The overall study and its experimental protocol were approved by the institute ethics committee of IIT Hyderabad (IEC Protocol No: IITH/IEC/2019/05/13). Toenails were collected from three communities, Sepakkam (13°16'37"N, 80°18'19"E), Athipattu Pudu Nagar (13°14'58"N, 80°17'54"E), and Avurivakkam (13°25'40"N, 80°16'19"E) situated 20 – 50 km from Chennai, Tamil Nadu, India. Sepakkam and Athipattu Pudu Nagar are situated in the Ennore suburb of Chennai. There are three power plants operating in the area: North Chennai Thermal Power Station (NCTPS, Capacity: 3 × 210 MW; 2 × 600 MW), Vallur thermal power plant (Capacity: 3 × 500 MW) and Ennore thermal power plant (Capacity: 2 × 60 MW; 3 × 110 MW). The two sites are located within 10 km of the power plants. Avurivakkam is located 37 km from Sepakkam and Athipattu Pudu Nagar. There was no industry in the vicinity but the community was located next to the Pulicat Lake, which is a brackish lagoon of area 759 km². The volunteers filled a consent form and a survey was conducted to collect the socio-demographic information including details on age, gender, income, education, rice and fish consumption per week, duration of residence, profession and water source of the three communities (Table S1). Analysis of metals concentrations in nails and their relation to the potential sources at each of the three sites will be addressed in another work and is beyond the scope of this work.

Ninety-seven toenail samples were collected from three communities, 36 each from Sepakkam and Athipattu Pudu Nagar and 25 from Avurivakkam. The toenails were clipped from all the toes. The collected samples were stored in metal-free double zip lock bags and analyzed in a metal-free lab environment.

A non-ionic detergent (Tween® 20, Croda International PLC) was used to clean toenail samples prior to metal(loid) analysis using a 1% solution for 30 minutes in a sonicator. Tween 20 is polyoxyethylene sorbitan ester and is a solubilizing and emulsifying agent²⁵. Samples with nail polish were cleaned with acetone before washing. The mixture was vortexed and the aqueous solution was removed. The samples were then soaked in 1% Tween 20 solution for a period of 2 days. After soaking, the aqueous solution was replaced with fresh 1% Tween 20 and sonicated for 30 minutes followed by washing with type 1 water (ultrapure water with resistivity > 18 MΩ-cm). The nails were then dried, weighed, and ready for portable XRF and ICP-MS analysis¹⁷.

2.2. Portable XRF analysis

The portable XRF device used in this study was a customized ThermoNiton XL3t GOLDD+ (Thermo Fisher Scientific, Billerica, MA) handheld XRF. The device operates at a 2-watt

power output, and we used settings of 50 kV and 40 μ A with a silver filter. The toenail samples were measured by placing all clippings over the x-ray aperture for 3-minutes. The calibration and analysis followed methods used in previous studies and accounts for variability in toenail mass and thickness^{17,24}. Briefly, we utilized a competing process through Compton scattering in order to normalize to the total size of clippings and any discrepancy in thickness of the toenails that may be influencing the measurements. The Compton scattering peak is primarily composed of characteristic x-rays generated from the x-ray anode and interacting with the sample before being collected at a slightly lower energy by the device's Si radiation detector. We fit the Compton scattering peak (~20 keV) and elemental peaks (Ni, Zn, As, Se, and Pb) using a Gaussian function with exponential background components to obtain net counts. Ni (7.48 and 8.26 keV), Zn (8.64 and 9.57 keV), As (10.54 and 11.73 keV), and Se (11.22 and 12.50 keV) were fitted using the K-alpha and K-beta lines respectively. Pb was quantified using the fitting from the L-beta line of 12.61 keV. The L-alpha line at 10.55 keV line was still fitted to remove the competing counts from the As 10.54 keV peak, but not used in the quantification, as this reduced the overall certainty of findings. Over all fittings, the average chi square goodness of fit parameter was 1.2 ± 2.6 (494 degrees of freedom). The net elemental counts were then divided by the Compton scattering counts to normalize the results. Following our previous work^{17,24}, we derived sample calibrations from lab made epoxy resin toenail sample doped with concentrations from 0 to 50 mg/kg of Ni, Zn, As, Se, and Pb. These samples were made with composition such that it mimicked nail properties for the purposes of x-ray absorption. Standards included differing thicknesses and clipping masses to accommodate variations in natural sample collection and allow for our calibration to include the potential uncertainty introduced during the normalization process for mass and thickness as outlined in our previous work^{17,24}.

2.3. Inductive coupled plasma mass spectrometry

An Agilent 7900 ICP-MS was used for the analysis of toenail samples. It has a robust plasma and Ultra High Matrix Introduction (UHMI) technology that enables the measurement of rare earth metals and metalloids with high sensitivity. Dried toenails were digested with concentrated nitric acid (0.01%) at 100°C for one hour⁶. The digested solution was cooled at room temperature and diluted to 10 mL with type 1 water. The aqueous solution was then analyzed using ICP-MS⁶.

Matrix blanks were prepared by replacing the sample with type 1 water. The method detection limit (*MDL*) was determined as follows:

$$MDL = t_C \times SD \quad \text{eq(1)}$$

where, t_C is 3.143 [the critical value obtained from a *t*-test at confidence level 0.01 and a degree of freedom 6 (i.e. $n-1$ where n is sample size)]. One matrix blank was run 7 times and standard deviation (*SD*) was calculated. Reported sample analyte concentrations were a minimum of 2.5 times higher than the method detection limit²⁶. The multi-elemental standard used for analysis was Elemental Scientific (ESI) Control Standard solution #26.

Stock solutions were prepared with concentrations ranging from 10 µg/L to 200 µg/L for all metal(loid)s.

2.4. Statistical analysis

Two analyses were used to compare results obtained from XRF and ICP-MS: Passing Bablok regression²⁷⁻²⁹ and Bland-Altman³⁰⁻³². Passing Bablok regression is a non parametric method that does not require normality of data obtained from the two methods and is robust in the presence of outliers. The method assumes there is a linear relationship between the two sets of values. This was checked using the cumsum test. The method fits the intercept and slope of a linear regression $y = a + bx$, and determines the respective 95% confidence intervals (CI)²⁹. If zero is not in the CI for a , there is a systematic difference (bias) between the two methods, if unity (one) is not in the CI for b , there is a proportional difference (bias) between the two methods. A reasonable sample size for Passing Bablok analysis has been suggested to be 50³³.

Bland-Altman analysis is also used to compare two different methods. It calculates the mean difference (bias) and a 95% CI between which the differences of the two methods would fall, thereby constructing the limits of the agreement. If y_1 is a particular measurement value from the first method and y_2 is the corresponding measurement value from the second method, a mean value of the two is calculated as $(y_1 + y_2)/2$ and the difference as $(y_1 - y_2)$. Then, differences in all sets of measurement values are plotted against all the corresponding mean values. The mean bias between the two methods was calculated as:

$$\bar{y} = \frac{1}{n} \sum_{k=1}^n (y_1 - y_2)_k \quad \text{eq(2)}$$

95% limits of agreement are calculated as mean bias plus or minus 1.96 times the standard deviation of the differences. If in a future analysis it is decided that expected differences in measurement values between the two methods fall within the 95% limits of agreement, then the methods can be used interchangeably. This analysis assumes that the differences of values obtained from the two methods are normally distributed.

Pearson's correlation coefficient (r) was calculated only as a means to assess the linearity between the concentrations of each metal(loid) measured by XRF and ICP-MS, and the deviation from the expected ideal 1:1 relation, using IBM SPSS statistics 20. It may be noted that correlation coefficient does not represent an agreement of the methods³². Calculation of r assumes that the values are normally distributed and do not contain outliers. The linear regression model was used to estimate beta, intercept and variance at 95% confidence interval. All obtained values were retained for all the statistical analyses³⁴.

3. Results and Discussion

3.1. Calibration and quantification

The calibration results of ICP-MS for target metal(loid) ions, nickel, zinc, arsenic, selenium and lead are given in Figure 1. The calibration curve has a regression coefficient of more than 0.99 for the metal(loid)s selected. The method detection limits are given in Table 1.

The residual standard deviation (RSD) obtained from multiple analysis ($n = 3$) of each of the standard solution concentrations used for calibration for each metal(loid) was less than 4%, for all metal(loid)s for all concentrations..

The XRF analysis was calibrated using nail phantoms as described by Specht et al. ¹⁷ and the calibration curves for each metal(loid) are given in Figure 2. A sample spectrum is presented in the Supporting Information (SI) Figure S1. The Ni calibration has a y-intercept due to inherent Ni in the XRF device collimation, but this should be accounted for in our quantification. Method detection limits are given in Table 2. The detection limit of ICP-MS is much lower than XRF, and should be considered prior to exposure assessment.

3.2. Correlation between XRF and ICP-MS data

The measured metal(loid) concentrations from the two methods are given in Table 3 (overlapping histograms in SI-Figure S2, and in SI section S1 for individual sites), the parameters obtained from the Passing Bablok regression are presented in Table 4 and Figure 3, the Bland Altman analysis in Figure 4, and for Pearson's correlation in Supporting Information (SI-section S2). The values obtained from ICP-MS and XRF were normally distributed for nickel and lead. For zinc, once we removed the highest measured value (880 mg/kg, compared to a median of < 105 mg/kg) the distribution became normal for both ICP-MS and XRF measured values. For arsenic, the distribution was lognormal only for ICP-MS data (SI section S3, Table S6). The differences between the measurements taken from ICP-MS and XRF were normal for nickel, zinc and lead. Therefore, Passing Bablok regression analysis is applicable for all elements (the relationship between ICP-MS and XRF measurements was linear), Bland Altman analysis for nickel, zinc and lead, and the classic Pearson's regression also for nickel, zinc and lead.

The average nickel concentrations quantified by XRF and ICP-MS were 156 mg/kg and 163 mg/kg, respectively. The 95% confidence interval (CI) of slope b of the Passing Bablok regression spans across one (median value of 1.00 with a 95% CI of 0.985 to 1.02), suggesting no proportional difference between the two methods across the entire measurement range. The 95% CI for a is between -4.23 and -9.56 with a median value of -6.51, suggesting a slight absolute bias in values obtained by the two methods. Regression results for individual sites are presented in SI Tables S7-S9 are largely consistent with the overall results in Table 4. There is a larger range of 95% CI in bias and the 95% CI crossed zero for one of the sites, Athipattu Pudu Nagar, meaning the XRF and ICP-MS analysis could be used interchangeably; however, the sample size was less than 50 ³³ and this interchangeability inference may be an artifact of a somewhat smaller sample size. The results were closer for other sites and there was no indication of site-specific performance. Bland-Altman analysis shows that the mean estimated bias is -7.04 mg/kg, consistent with the absolute bias determined from the Passing Bablok analysis, and the 95% limits of agreement were 8.58 mg/kg and -22.6 mg/kg (Figure 4). Linear regression analysis also showed a high correlation (Pearson's correlation coefficient $r = 0.996$, $R^2 = 0.991$, $slope \approx 1$; SI-Table S5 and Figure S2).

The widest concentration range was detected for zinc (XRF = 0 – 887 mg/kg and ICP-MS = 9.35 – 893 mg/kg). Most zinc concentrations were below 200 mg/kg. Passing Bablok

analysis revealed no proportional difference (95% CI for slope b spanned across 1) between the two methods but there was a small systematic difference (Table 4). The result from individual sites (SI-Table S7-S9) were similar, but with a larger 95% CI, and XRF and ICP-MS were in agreement for Athipattu Pudu Nagar and Sepakkam, and there was a small absolute bias for Avurivakkam. The overall bias estimated from Bland-Altman analysis was -7.29 mg/kg with a 95% limits of agreement of -28.4 mg/kg and 13.8 mg/kg (Figure 4). Concentrations determined by XRF and ICP-MS were also highly correlated in the linear regression analysis ($r = 0.993$, $R^2 = 0.986$, $slope = 0.992$).

Average concentrations of selenium determined by XRF and ICP-MS were 5.62 mg/kg and 6.54 mg/kg, respectively. Passing Bablok analysis showed a regression slope of 0.928 (95% CI: 0.878 to 0.945) and no absolute bias, -0.029 mg/kg (95% CI: -0.045 to 0.00) when the entire range of values was considered. However, the majority of samples ($n = 80$) had values below 2 mg/kg. When we removed all values greater than 2 mg/kg, the regression slope decreased to 0.835 (95% CI: 0.694 to 0.916) and the intercept to -0.003 (95% CI: -0.029 to 0.013 mg/kg). This suggests a proportional difference in measurements made by the two methods and a no absolute bias at low concentrations. When we only considered values above 2 mg/kg ($n = 17$), the 95% CI for the regression slope and intercepts contained unity and zero, respectively. The proportional difference was more pronounced for Sepakkam (Table S7, slope of 0.628 with a 95% CI of 0.484 to 0.881) probably because the lower concentrations of selenium detected in its population by the XRF, and the 95% CI of slope and bias were close to one and zero for Avurivakkam, likely in part due to the higher concentrations measured by the XRF (SI-Table S4 and Figure S5). Spearman's correlation, when used just to assess the deviation from a 1:1 line, was 0.999 ($R^2 > 0.998$, $slope = 0.970$) when the entire range of values was considered, but fell to $r = 0.744$ ($R^2 = 0.554$, $slope \approx 0.577$) when we consider values less than 2 mg/kg.

Arsenic concentrations varied between below detection limit (BDL) and 3.80 mg/kg with an average concentrations of 0.702 mg/kg and 1.19 mg/kg measured by XRF and ICP-MS, respectively. The Passing Bablok slope was 0.253 (95% CI: 0.037 , 0.614) and the intercept was -0.057 (95% CI: -0.227 , 0.00) suggesting no absolute bias but a large proportional bias between the two methods. Both slope and intercept parameters were zero for Avurivakkam because arsenic concentration in all except three of the twenty five toenail samples was recorded as zero by the XRF (see SI-Figure S6). The performance difference seems to be related to the ability of XRF to measure low values rather than the actual difference in concentrations among the sites. This is likely compounded by the difficulty in fitting algorithms to address the difference between lead and arsenic peaks, which in our case has raised the detection limit for arsenic and potentially made measured concentrations in some of these nails lower than the limit of detection for the device. Spearman's correlation, when used just to assess the deviation from a 1:1 line, was weak ($r = 0.491$, $R^2 = 0.241$, $slope = 0.354$).

Contrary to what was observed for selenium and arsenic, measurements of lead from the two methods showed no proportional difference ($b = 0.963$, 95% CI: 0.919 to 1.001), and a slight absolute bias of -0.160 (-0.092 , -0.216) (Table 4), even though the values were always lower than 4.5 mg/kg with a mean concentration of 1.44 mg/kg. Parameter values for

individual sites were largely consistent with the parameters in Table 4 for all sites combined. Mean absolute bias from the Bland-Altman analysis was -0.203 mg/kg with a 95% limits of agreement of -0.651 mg/kg and 0.244 mg/kg (Figure 4). Spearman's correlation was high ($r = 0.974$, $R^2 = 0.949$, $slope = 0.945$).

The portable XRF used in our work was capable of making very low level lead measurements because lead has the lowest elemental detection limit with the XRF methodology used in this study. XRF calibration plays a significant role in the accuracy and precision of measured elemental concentration. There has been literature on various calibration methods used for improving metal(loid) quantification^{20,21}. The portable XRF used in the study was calibrated by fitting Compton scattering peak against the standard nail phantoms doped with known elemental concentration. Secondary absorption or enhancement of target wavelengths by atoms of other elements is one of the most important sources of bias in XRF measurements¹⁴. Fluoresced characteristic x-ray is absorbed by another atom, and this atom may potentially generate additional x-rays. This may become problematic at low concentrations of target analyte. The limitations of the XRF are thus all focused on the detection capabilities, which can be increased using a higher powered device, with a longer measurement time, or both. The detection limits can be further improved by calibration, using a higher power device and increased measurement time^{17,24}.

Portable XRF has been widely used for elemental analysis but limited studies have been conducted on validation of its efficacy with respect to ICP-MS for human sampling. A recent study has reported a high correlation between the portable XRF and ICP-MS values for manganese but less correlation for lead in nail due to lower concentrations¹⁷. A study on arsenic concentration of dried baby shrimp³⁵ stated a high correlation between arsenic concentrations quantified by portable XRF and ICP-MS. The lowest concentration reported in that study was 4 mg/kg, but in the present study the concentrations were much lower than 2 mg/kg. These findings suggest portable XRF may perform better as a quantification tool for arsenic concentrations higher than 2 mg/kg. A combination of XRF and ICP-MS techniques have been implemented for evaluation of elements accumulated in leaf due to dust (High Resolution ICP-MS) and in various parts of *Couroupitaguianensis* required for soil nutrient reclamation, respectively^{36,37}. Laser Ablation (LA-) ICP-MS and XRF have been used for discriminating the overall composition of document paper³⁸. XRF techniques are also widely used for sediment metal(loid) analysis³⁹.

It has been previously reported that toenails arsenic concentrations are significantly correlated to urinary arsenic and total body arsenic levels⁴⁰. Although toenails have not been validated as biomarkers for arsenic they provide reliable measure of arsenic exposure⁴¹. Selenium and zinc concentrations in toenails have reproducibility for long-term exposure⁷. Salcedo-Bellido et al.⁴² have concluded that 7-12 months of nickel and lead exposure can be detected in the toenails. The purpose of the presented work was to evaluate the usefulness, and possible limitations, of portable XRF in measuring metal(loid) concentrations in human nails. Results can be interpreted considering information obtained from such aforementioned exposure-biomarker studies.

Overall we find that the portable XRF can be used as an efficient and a high throughput tool to detect exposure of humans to metal(loid)s. Passing Bablok regression of the measurements of nickel, zinc and lead suggested XRF and ICP-MS analyses methods had no proportional bias and a small absolute bias. The two methods could be used interchangeably for these elements. Limits of agreement from Bland-Altman analysis are presented and may be used to assess what limits will be acceptable in future studies. Future applications of the XRF device for mass screening of humans in potentially high exposure settings, such as occupational exposure in metal(loid) industries or residential exposure in vicinities of high-metal(loid) emitting industries, would take advantage of the convenient new measurement methodology.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Synopsis:

Portable x-ray fluorescence is an effective tool for exposure assessment of metal exposures, especially for community or in-field studies.

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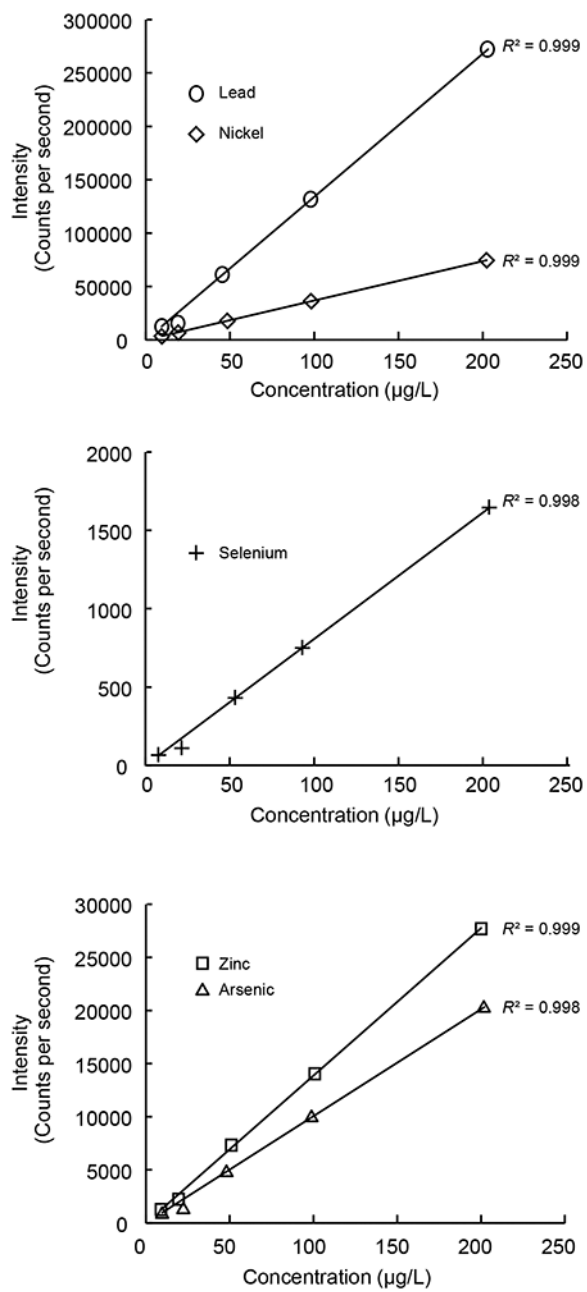


Figure 1.
Calibration curves for ICP-MS

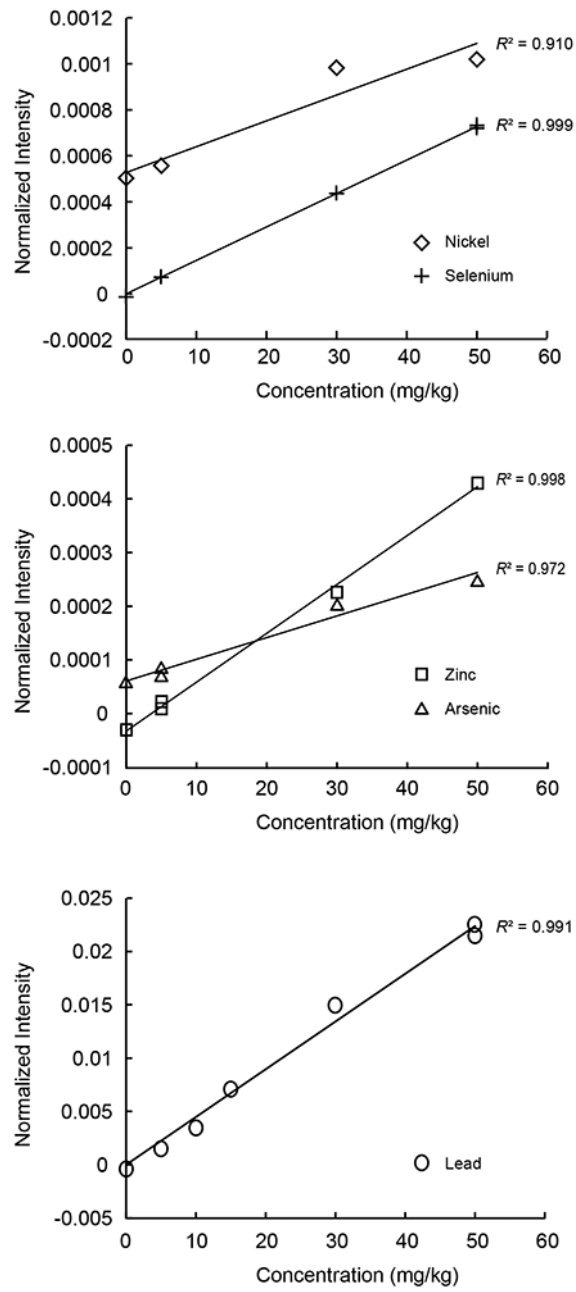


Figure 2.
Calibration curves for XRF.

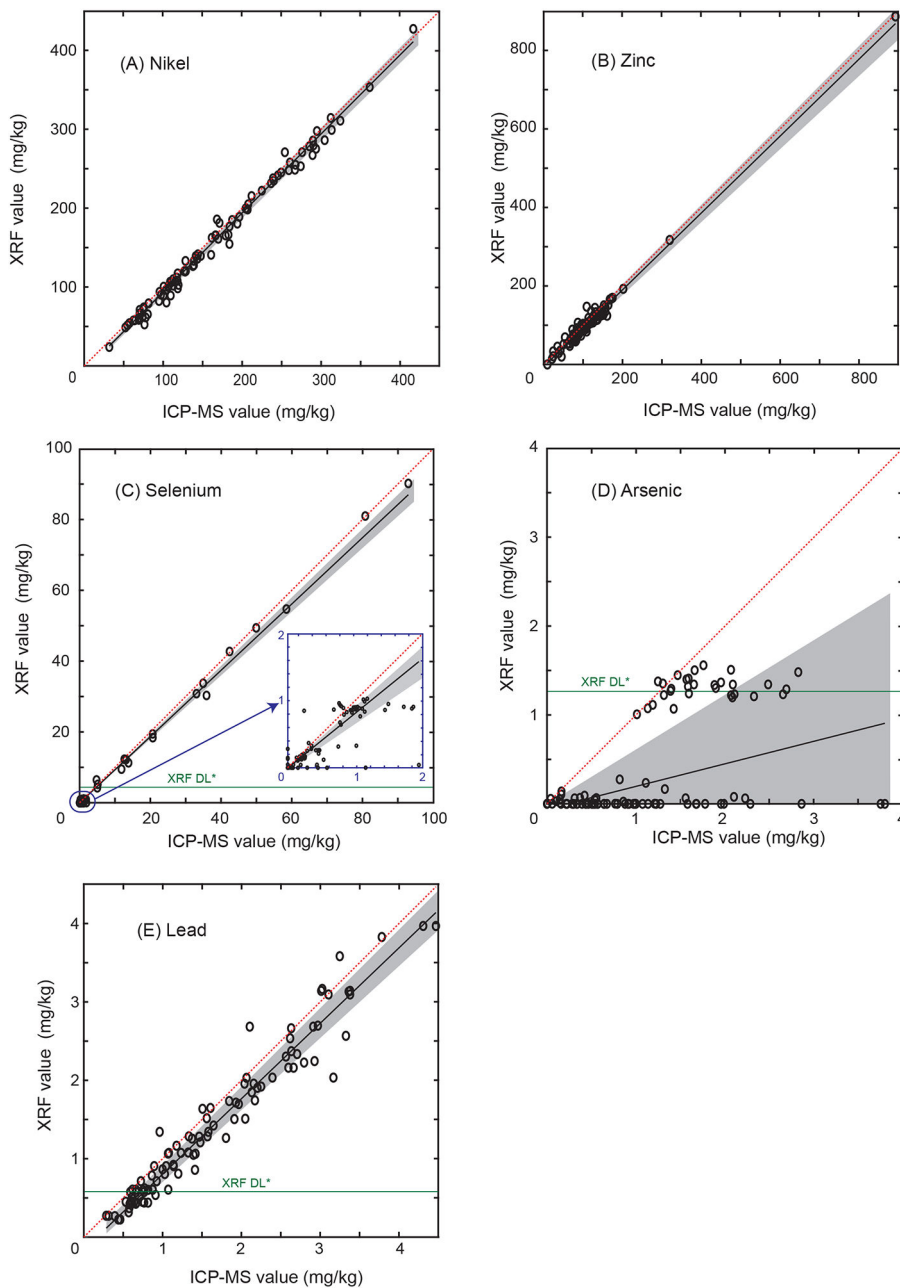


Figure 3. Passing Bablok regression curve. Dotted red line is the 1:1 line. Shaded band represents the 95% confidence interval of the slope. The solid green line denoting XRF DL* represents the detection limit of XRF calculated from its calibration parameters.

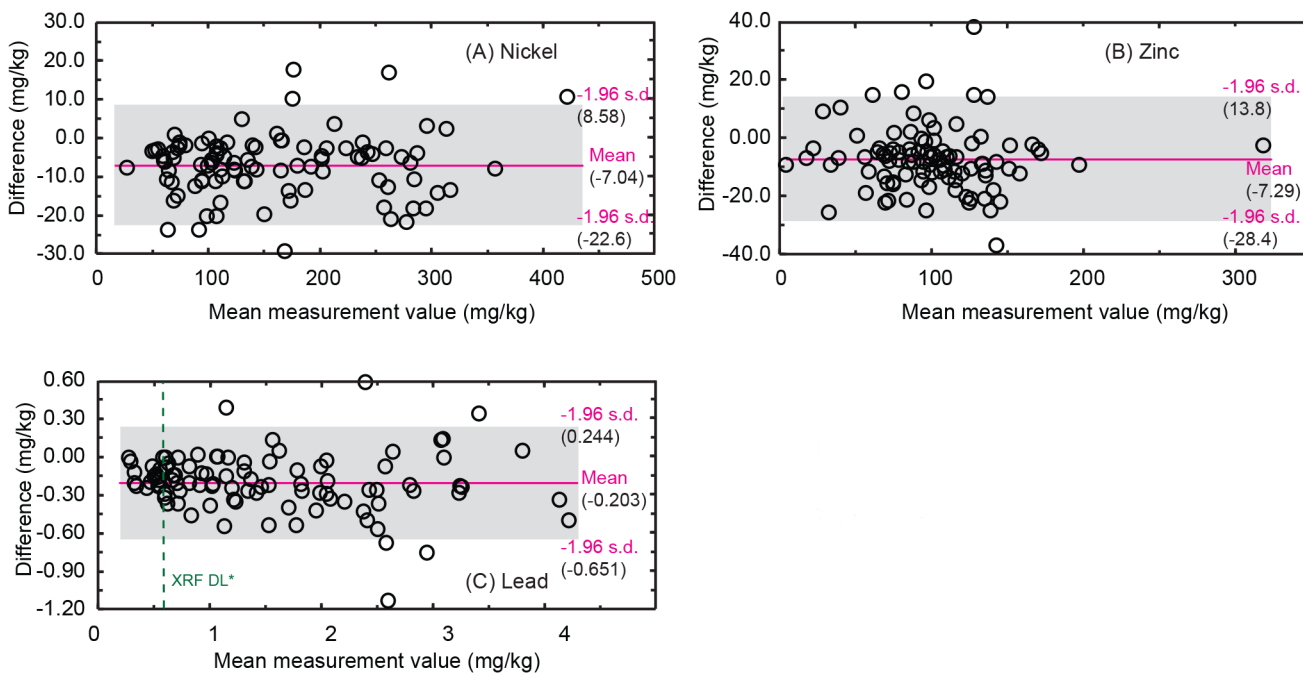


Figure 4. Limites of agreement of the two methods obtained using Bland-Altman analysis. Limits are represented as the shaded region (s.d. = standard deviation). The vertical dotted green line denotes the detection limit of XRF determined from the calibration parameters (XRF DL*).

Table 1:

QA/QC and method detection limits for ICP-MS for target metals

Metal Ions	Method Blanks ($n = 7$)		Method Detection Limit (ppb, $\mu\text{g}/\text{kg}$) ¹	Standard Recovery (%) ($n = 7$)	R^2
	Mean	Standard Deviation			
Ni	1.62	0.923	2.90	97.5 \pm 2.23	0.999
Zn	3.20	3.21	10.1	98.6 \pm 4.25	0.999
As	0.248	0.058	0.181	99.02 \pm 2.14	0.997
Se	0.837	0.316	0.994	97.8 \pm 11.3	0.997
Pb	1.21	0.213	0.670	96.2 \pm 3.85	0.998

¹: Method detection limit calculated as three times the standard deviation.

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Table 2:

Method detection limits for XRF

Metals	XRF Method Detection Limit (ppm, mg/kg) ^I	R ²
Ni	3.53	0.910
Zn	2.87	0.998
As	1.27	0.972
Se	4.60	1.00
Pb	0.58	0.991

^I: Calculated from the calibration line of the XRF. This limit calculated from calibration parameters can be dependent on sample properties like mass and composition, which vary from sample to sample.

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Mean, standard deviation (S.D.), maximum, minimum and median concentrations (mg/kg) corresponding to each metal measured in toenails.

Table 3:

Concentrations	Nickel		Zinc		Arsenic		Selenium		Lead	
	ICP-MS (mg/kg)	XRF (mg/kg)	ICP-MS (mg/kg)	XRF (mg/kg)	ICP-MS (mg/kg)	XRF (mg/kg)	ICP-MS (mg/kg)	XRF (mg/kg)	ICP-MS (mg/kg)	XRF (mg/kg)
Mean	163	156	113	105	1.19	0.702	6.54	5.62	1.64	1.44
S.D.	83.9	84.5	90.8	90.7	0.83	0.636	16.6	15.6	0.998	0.971
Median	139	133	102	95.6	1.11	1.04	0.775	0.369	1.40	1.23
Maximum	417	427	893	887	3.80	1.56	92.9	90.2	4.47	3.97
Minimum	31.8	23.9	9.35	BDL ⁱ	0.006	BDL	0.019	BDL	0.285	0.225

ⁱ: BDL = below detection limit

Statistical parameters from the Passing Bablok analysis of XRF and ICP-MS measurements. Results are the parameters of the equation $y = a + bx$, where x is the ICP-MS measurement and y is the XRF measurement expressed as median and 95% confidence interval (CI).

Table 4:

Element	<i>a</i>		<i>b</i>	
	median	(95% CI)	median	(95% CI)
Ni	-6.51	(-4.23, -9.56)	1.00	(0.985, 1.02)
Zn	-5.89	(-0.943, -9.22)	0.980	(0.930, 1.02)
Se *	-0.029	(-0.045, 0.000)	0.928	(0.878, 0.945)
As	-0.057	(-0.227, 0.000)	0.253	(0.037, 0.614)
Pb	-0.160	(-0.092, -0.216)	0.962	(0.919, 1.00)

* For concentrations less than 2 mg/kg (n = 80): a = -0.003 (-0.029, 0.013), b = 0.835 (0.694, 0.916). For concentrations greater than 2 mg/kg (n = 17): a = -0.682 (-1.73, 0.151), b = 0.980 (0.933, 1.02).