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A Comparison of Reproducibility of Inductively Coupled Spectrometric Techniques in Soil Metal Analyses

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ABSTRACT: Precise estimation of metals in samples remains a challenge as a result of analytical biases and errors, which occur at sample collection, preparation, and measurement stages. A poor understanding of the nature and occurrence of these errors further aggravates this challenge. This study aimed at comparing the effectiveness of inductively coupled plasma (ICP) mass spectrometry (MS) and optical emission spectrometry (OES) techniques in quantifying metals from contaminated soils of Roundhill landfill vicinity. Using statistical tools, the study evaluated biases of the 2 methods. High coefficients of variation were realized for V, Cr, and Pb concentrations varied at various sampling sites. Concentrations of elements obtained using the 2 methods had no significant differences using *t*-test analysis. Definitive agreement for the 2 methods was observed for V, Cr, Co, Ni, Cu, Zn, Sr, and Pb concentrations, whereas the concentrations of Mg, Ca, Ti, Mn, and Fe showed some deviations in their regression lines. Spectral, systematic, memory, and carry over errors could be attributable to these deviations. The errors promote chelation and adsorption of ions in samples to form insoluble compounds that cannot be quantified. Overall, ICP-MS had greater sensitivity than ICP-OES in trace elements analysis compared with major elements.

KEYWORDS: Bias, errors, spectrometry, metals, reproducibility, soils

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Introduction

Analytical biases and errors in metal analyses present in various matrices (such as plants and soils) are important, yet less understood and unrecognized aspects during assessment of pollution in such environmental samples.¹ These limitations occur when concentrations of same sample replicas differ when quantified at different time intervals and using different techniques.^{2–4} A number of causatives have been attributed to this phenomenon including sample-matrix chemistry, sample contamination at the field or in the laboratory, and analytical bias and sensitivity differences in used measurement techniques.^{2,3} Sediments and soils have been reported as the most difficult environmental samples to quantify for metal analysis using spectrometric techniques.⁵ The analysis difficulties are due to the complex nature of soils, particularly its multi-elemental nature with soluble and insoluble components^{5,6} and the matrix effect often associated with soils' geographical location, lithologic and anthropogenic factors.^{6–8} Soil matrices could change the nature of plasma and result to spectral component interferences.^{5,9} Matrix effects occur when absorptivity change, elemental distribution and ablated mass of same soil samples result in different concentrations and signal responses during analysis.⁴ These effects often disrupt a soil's speciation and composition and ultimately the quantifiable elements in a given sample.^{5,7} According to Woodard et al,⁹ who assessed the accumulation of metals in roadside soils of Franklin county (Massachusetts),

these limitations result to false negatives and positives, non-detection, and overestimation of elements during analysis.'

Inductively coupled plasma optical emission spectrometry (ICP-OES) also known as ICP-atomic emission spectroscopy (AES) is vulnerable to errors that result from analytical processes such as sample collection, preparation and storage, and instrumental techniques.¹⁰ At collection and storage, analytical errors result from adsorption of metal ions and their subsequent loss due to longer freezing periods, whereas in sample preparation, cross-contamination is a likely occurrence.^{2,3,11} Errors that occur during measurement could be due to sample composition and result in isobaric interferences.¹¹ A review by Hoenig¹² on the considerations made during analyses of environmental (soils, sediments, plants, food, and animal) samples highlighted the need to understand these errors as a preliminary counter measure. Velitchkova et al¹³ applied the Q-concept to quantify spectral interferences and reported ICP-OES vulnerable to background enhancements of the spectrum for elements identified between 200 and 320 nm wavelengths. The interferences are pronounced when linear plotting of calibration curves is done, which affects resultant intercepts.^{11–13} In soil analyses using ICP-OES, it is even more difficult to assess the magnitude and type of interference due to its complex nature.^{5,7} Specific metal analysis using ICP-OES has confirmed the presence of such errors as reported in a metal analysis of soils from Wyoming, USA.¹⁴ An analysis of cadmium



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using ICP-OES was deemed as inaccurate due to spectral interferences that caused overestimation and non-detection in some cases.⁶ Similarly, Velitchkova et al¹³ reported the presence of spectral interferences when assaying for arsenic, mercury, selenium, and titanium in Bulgarian soils using ICP-OES.

On the other hand, ICP-mass spectrometry (ICP-MS) has been used as an alternative to ICP-OES due to its high sensitivity and analytical precision.^{10,2-13,15} However, it is not free from analytical errors such as matrix complex effect and drift errors.¹¹ In the latter, errors result due to changing responses of ICP-MS equipment with concentration changes and time as its ambient temperature fluctuates.¹¹ Drift errors decrease the sensitivity of the equipment resulting in under- and overestimation of analytes and is dependent on the matrix.¹³ In complex analytes such as sediments, plants, and soils, these errors lead to faulty sample transport and affect the total analyte recovery and yield particularly in major elements that are in high concentrations.^{11,16} Matrix complex effect of ICP-MS, on the other hand, suppresses the analyte, but it can be eliminated by matrix-matching their standards and unknowns.¹⁰ Although detection capacities of ICP-MS are in most cases superior to ICP-OES to the tune of 3 orders,¹⁶ they could be too high for some soil matrices whose metal composition has been enhanced by anthropogenic and lithologic processes.¹⁰ The errors associated with solvent and concomitant species' matrix effect, insufficient sample introduction, and in some case spectral interferences reduce ICP-MS's effectiveness in trace metal analysis of complex environmental samples such as soils.¹⁶

Therefore, ICP-MS and ICP-OES have divergent strengths and weaknesses in analyses of trace elements as observed from comparative studies. For instance, a soil analysis by Franklin et al¹⁵ in South Carolina deemed ICP-OES results of Cd to be erroneous compared with ICP-MS, whereas those of Al, Be, Co, Li, Ni, Ru, V, and Zn were comparable. At near background level, soil Cd levels could not be determined accurately with ICP-OES and gave unreliable values compared with ICP-MS.⁵ ICP-OES gave higher values of macronutrients such as P, K, and Mg compared with ICP-MS in a comparative analysis of wood ashes in France.¹⁷ ICP-OES was reported as a superior analytical technique for major elements in oysters from Lake Charles (USA) compared with ICP-MS that was complex and required serial dilution of samples although it had better results for rare trace elements.¹⁸ Cr, Ni, Cu, Zn, Cd, and Pb levels obtained with the 2 techniques had acceptable linearity and a t-criterion technique did not show any significant differences for all samples.¹⁹ In light of differences in these comparative studies and with the site-specific nature of environmental matrices, the current study sought to (1) assess the comparative effectiveness of 2 spectrometry techniques in multi-element analysis of landfill contaminated soils and (2) quantify resultant biases and errors using statistical tools to get an in-depth understanding of their sources. This study hypothesized that ICP-MS and ICP-OES are effective methods for determining metal concentrations in soils.

Materials and Methods

Soil sampling and processing

Soils were sampled from Roundhill landfill located in South Africa's Eastern Cape province at Buffalo City Municipality (longitude 27°37'26.20"E, latitude 32°53'13.66"S) as shown in Figure 1A and B. The area has a gentle slope (3.5°), was previously used as grazing land, and is located between Buffalo river and Nahoon river catchments and near a national road.²⁰ The area is characterized as Jurassic age dykes, dolerite sheets, and Karoo sequence of sediments.²⁰ Location of the landfill is in an area with positive water balance and can generate leachate. Ground water potential of the area is low with a >40-m depth and borehole yields of <1 L/s. Soil profile has O, A, B, C, and R horizons comprising scrub vegetation, silty-sand, clay, and rocky layers as shown in Figure 1D.²¹ The landfill receives more than 500 tons of waste daily, which includes domestic waste, plastics, papers, ash, metal scrap, used tires, building, and construction waste.²¹ Soils were collected from 9 sampling sites based on their location from the landfill facility and at 3 different soil depths: 30, 60, and 100 cm for comparative assessment of pollution (Figure 1C). These depths were selected as they fall under the surface and subsurface horizons that are vulnerable to leachate infiltration unlike the substratum and bedrock that are undulated.²⁰ A GPS was used to locate the sampling sites and soils were collected using an auger and emptied in plastic bags for transportation. They were oven dried at 105°C for 12 hours and stored for analysis of metals including Mg, Ca, Ti, V, Cr, Mn, Fe, Co, Cu, Zn, Sr, and Pb.

Microwave acid digestion

Soil samples to be analyzed by ICP-MS and ICP-OES require acid digestion to ensure metal dissolution and extraction. This study used the EPA method 3051A to digest soil samples in a microwave.²² This aqua regia technique does not dissolve samples in totality but decomposes them to separate soluble elements from insoluble silicate matrix, hence lowering the detection limits of analytes and dissolved solid concentrations.¹⁶ In this case, 1 g of dry soil that was pre-passed through a 2-mm sieve was dissolved in 1 mL hydrogen peroxide, 2 mL hydrochloric acid, and 9 mL nitric acid in a Teflon vessel and allowed to react for 5 min before sealing it. The vessels were transferred to a vessel liner and heated at 180°C for 5.5 minutes before holding for 9.5 min and thereafter cooling them. The digested content was then emptied to a plastic container, labeled and stored at 4°C for analysis. A total of 100 µL of each of the 27 sample digestates were drawn and diluted to 10 mL using deionized water for analysis in both ICP-OES and ICP-MS.

Calibration

Calibration that involves generation of linear responses between a particular element's concentration and ICP-MS/OES instrument was done using a set of standards and blanks

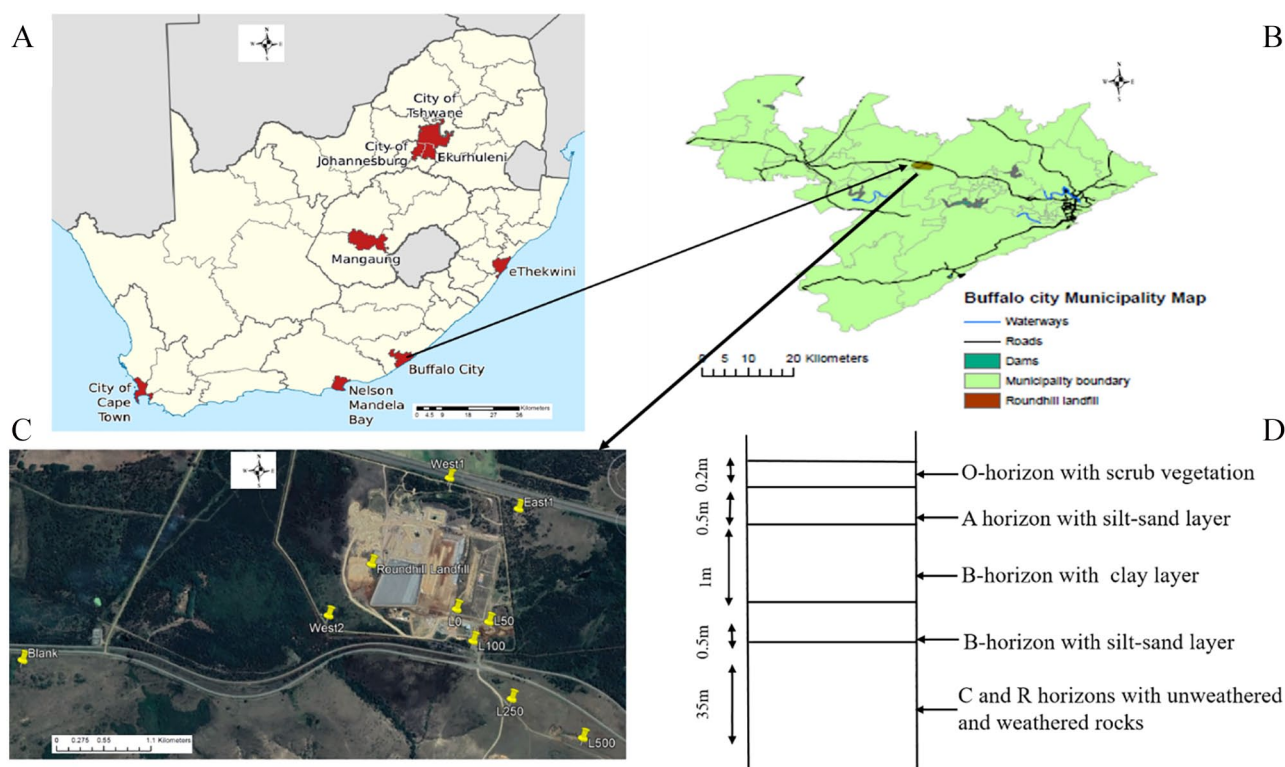


Figure 1. Description of the study area showing (A) map of South Africa, (B) the Buffalo city municipality, (C) the sampling sites, and (D) the description of area soil profile.

made using deionized water and reagents (HNO_3 , HCl , H_2O_2) used in microwave acid digestion. In ICP-OES, a matrix-matched solution of 1% nitric acid was used as the calibration solution and calibration concentrations ranged from 0 to 5 ppm for all analyzed elements. Standards used in preparing the calibration curve include 0, 0.1, 0.25, 0.75, 1, 2.5, and 5 ppm as described by Taylor¹⁰ and Hoenig.¹² In ICP-MS analysis, multi-element standard of high purity in 1% nitric acid was used as the calibration solution. The calibration curve covered 0 to 100 ppb for all analyzed elements. Standards to prepare the calibration equation had 0, 10, 25, 50, 75, and 100 ppb concentrations. Internal standards were spiked in calibration solution, blanks, and samples to serve as ionization buffers and monitor effects on analytes during calibration. For ICP-OES, Y and Cs were the internal standards unlike ICP-MS that used a combination of Bi, In,⁷ Li, Sc, Y, and Tb standards.¹⁸

Instrumentation

The Agilent 7500ce ICP-MS and the PQ 9000 Elite ICP-OES were used for this analysis. The main parts of the instruments are shown in Figures 2 and 3. ICP-OES (Figure 2) has a carrier gas tube and a torch made of a quartz tube and connected to a radio-frequency (RF) generator. Argon is introduced to the torch and RF is applied to create a magnetic field and produce ions and electrons. The resultant current flow heats the gas so that once sample introduction is done via the nebulizer, it is converted to aerosol and directed to the torch.^{10,18}

Light emitted by atoms of metals from samples in plasma is converted to quantifiable electrical signals.

ICP-MS (Figure 3) comprises an ion source (ICP) and an interface system with sampling, pumping and skimming cores, ions lens, a detector, and MS.¹⁶ Samples are introduced through the injection system and converted to ions under high temperatures and low pressure. Using a quadrupole system, metal elements are detected under high sensitivity through a peak hopping system to quantities below parts per billion.¹⁸

Digested soils samples were filtered, diluted, and assayed using the 2 instruments. After analysis, the final concentrations of each element were determined using equation 1:

$$\text{Metal concentration (mg/kg)} = \frac{\text{ICP - MS / ICP - OES concentration} \times \text{digestate volume} \times \text{dilution factor}}{\text{Weight of digested sample}} \quad (1)$$

where ICP means inductively coupled plasma, MS and OES represent mass spectrometry and optical emission spectrometry, respectively.

Statistical analysis

Three methods were used to compare concentrations of metals obtained by both ICP-OES and ICP-MS: (1) coefficient of variation (CV), (2) *t* test, and (3) linear regression analysis. CV calculated as a percentage ratio between the SD and means of

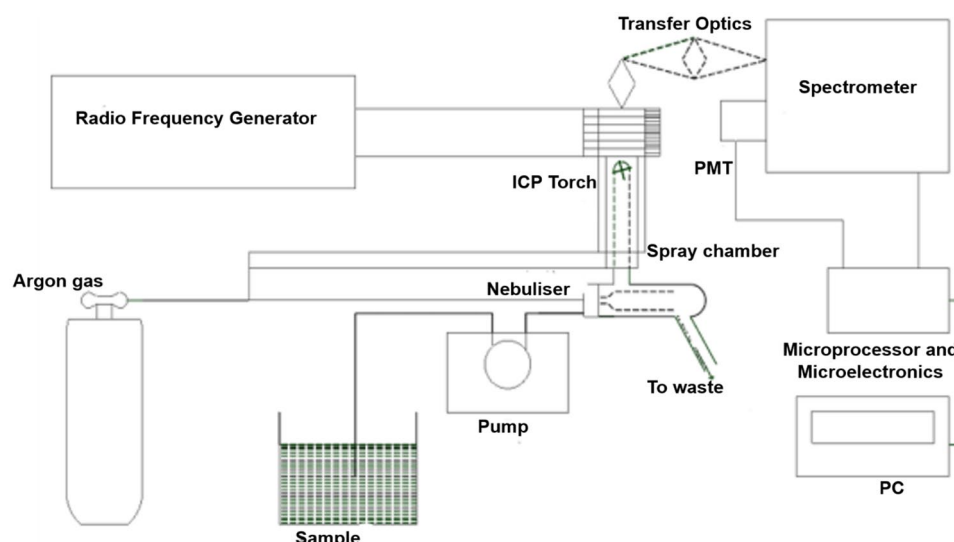


Figure 2. Schematic of a typical ICP-OES system. ICP-OES indicates inductively coupled plasma optical emission spectrometry; PMT, photo-multiplier tube; PC, personal computer.^{10,18}

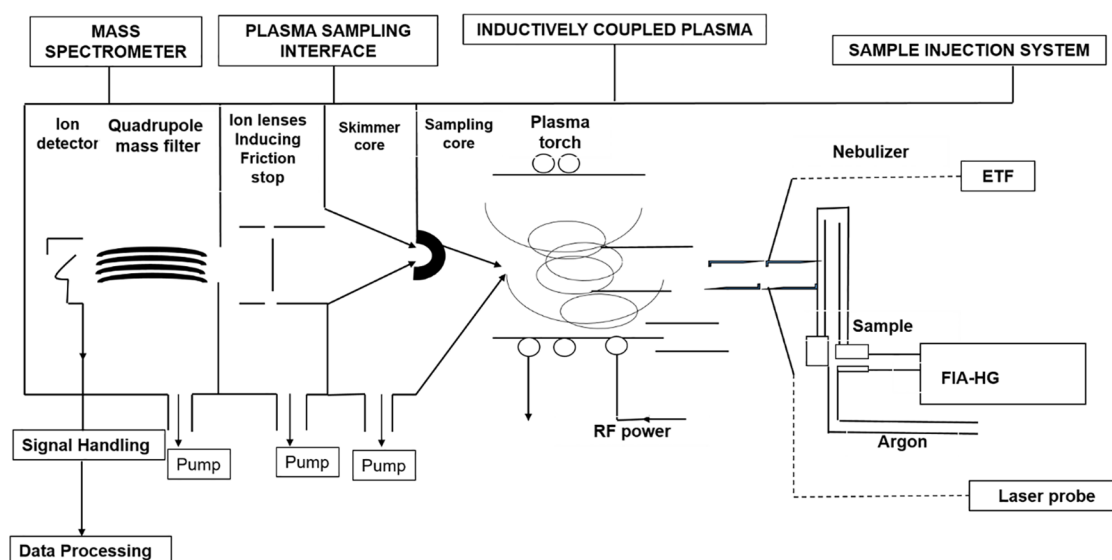


Figure 3. Schematic of a typical ICP-MS system. ICP-MS indicates inductively coupled plasma mass spectrometry; ETF, electro-thermal vaporization; FIA-HG, flow injection analysis-hydride generation; RF power, radio-frequency power.^{16,18}

the various elements. The method has been used to compare spread and variability of concentrations determined by spectrometry methods.¹⁹ A t test, which assumed equal variances assessed any significant differences of mean concentrations obtained from the 2 methods by comparing their tabulated t value with that of 95% significance level. Ahmed et al²³ and Maliki et al²⁴ did a similar statistical manipulation to compare metal analysis by different techniques. Linear regression analysis was used to correlate results of the 2 methods. Such comparisons have been used to compare results of metal analysis as documented by Helaluddin et al,²⁵ Han et al,²⁶ and Sneddon and Vincent.¹⁸ Resultant regression equations were assessed for any deviations from definitive relationships ($y=x$) and R^2 values of 0.7 and above were deemed as acceptable relationships of the methods.²⁷

Results and Discussion

Soil properties

ICP-OES and ICP-MS results were compared using descriptive statistics as shown in Table 1. Fe levels were the highest compared with other elements. The local geology comprising dolerite sheets that are rich in Fe explain the observed trend.²⁰ Means of most elements determined by ICP-OES were higher compared with ICP-MS. Standard deviation values of the 2 methods were high and depicted great dispersion of concentrations in the various soil sampling sites for all elements.

CV analysis

The percentage CV values of various elements are shown in Table 2. CV values for V, Cr, and Pb were above 100% because

Table 1. Comparison of ICP-OES and ICP-MS results of metal concentrations in soil extracts using their means and standard deviation.

VARIABLE	ICP-OES MEAN (MG/KG)	SD	ICP-MS MEAN	SD
Mg	6787.8	2721.4	6215.3	2166.7
Ca	13728.3	12301.9	10547.6	11913.8
Ti	9783.7	3697.1	9651.6	3708.5
V	436.6	440	435.6	439.7
Cr	1337.7	1375.4	1335.1	1374.8
Mn	16401.3	11114.9	8991.5	9673.9
Fe	174755.8	45006.5	155268	42093
Co	453	408.4	481.6	438.5
Ni	356.9	188.3	354.3	188.2
Cu	224.7	108.3	219.4	104.5
Zn	160	112.1	159.7	112.1
Sr	181.2	134.2	179.9	134.6
Pb	46.3	64.9	46.1	64.9
Minimum	46.3	64.9	46.1	64.9
Maximum	174755.8	45006.5	155268	42093

Abbreviations: ICP, inductively coupled plasma; MS, mass spectrometry; OES, optical emission spectrometry.

their SD exceeded the mean. These observations rendered the mean meaningless considering the high dispersion around it and are attributable to the huge variation in the data set as well as a number of inherent interferences for specific elements during analysis. According to Paya-Perez et al,¹⁹ inherent interferences of some elements such as Zn were attributable to CV values greater than 100% in a comparative ICP-MS and ICP-OES study on soil pollution in Abardeen, UK. Zhao et al²⁸ suggested that soil's complex nature could be the reason for CV values of beyond 100% for Ni and Cr in Chinese soil-rice systems using atomic spectroscopy. In both analytical techniques, CV values of Ti and Fe were the lowest, whereas values of Co, Zn, Ni, and Sr were relatively the same, which could infer to the ability of the 2 techniques to quantify these elements precisely. Mean concentrations, SD, and CV values of Mn and Ca showed significant differences that point to ICP-OES having better precision to analyze the elements compared with ICP-MS. This could be because of the latter's high sensitivity to trace element detection in low concentrations compared with major elements like Mn and Ca unless higher dilution factors are applied. Sneddon and Vincent¹⁸ agreed with these suggestions claiming that ICP-MS is preferable if elements in specific extracts are expected in low amounts compared with ICP-OES that can detect higher amounts without sample dilution. Furthermore, CV differences of Mn and Ca could be due to ICP-MS's vulnerability to drift effects, which lead to faulty sample uptake and subsequent underestimation of elemental concentrations

Table 2. CV values of various elements analyzed by ICP-OES and ICP-MS.

VARIABLE	CV% (ICP-OES)	CV% (ICP-MS)
Mg	40.1	34.9
Ca	89.6	112.9
Ti	37.8	38.4
V	100.8	101
Cr	102.8	103
Mn	67.8	107.6
Fe	25.8	27.1
Co	90.2	91.1
Ni	52.8	53.1
Cu	48.2	47.6
Zn	70.1	70.2
Sr	74.1	74.8
Pb	140.2	140.6

Abbreviations: CV, coefficient of variation; ICP, inductively coupled plasma; MS, mass spectrometry; OES, optical emission spectrometry.

compared with ICP-OES. Murphy and Vetter¹¹ reported a similar tendency of the equipment in a comparative analysis of Cd levels in dietary supplements and breakfast cereals using the 2 methods.

Table 3. Results of *t*-test comparing ICP-OES and ICP-MS means of various elements.

VARIABLE	MG	CA	TI	V	CR	MN	FE	CO	NI	CU	ZN	SR	PB
<i>P</i> value	0.4	0.34	0.08	0.98	0.99	0.01	0.11	0.8	0.96	0.86	0.99	0.97	0.99

Abbreviations: ICP, inductively coupled plasma; MS, mass spectrometry: OES, optical emission spectrometry.

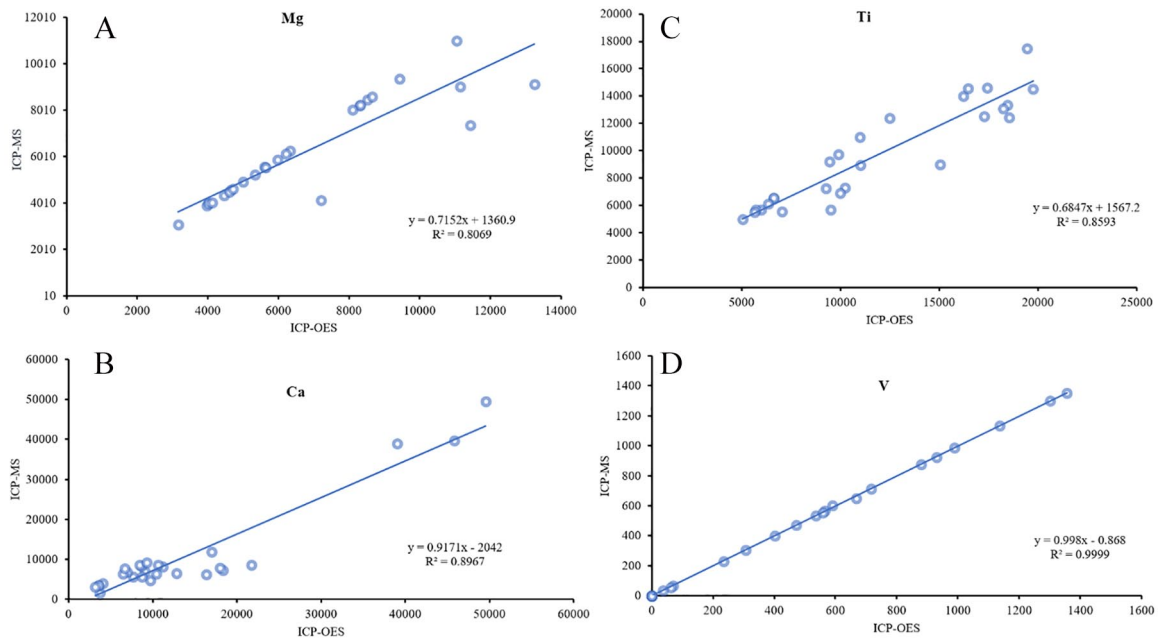


Figure 4. Regression results for ICP-MS and ICP-OES for (A) Mg, (B) Ca (C) Ti, and (D) V. ICP-MS indicates inductively coupled plasma mass spectrometry; ICP-OES, inductively coupled plasma optical emission spectrometry.

t-test analysis

The mean concentrations of various elements for the 2 techniques were compared using *t*-test ($\alpha=0.05$) as shown in Table 3. This method has been used in comparative analysis of methods for metals analyses as documented by Maliki et al²⁴ in a comparative study of XRF and ICP-MS for Pb analysis. Similarly, Nardi et al²⁷ used the method to compare metals in foods using ICP-MS and atomic absorption spectroscopy (AAS) techniques. The *P* values of assayed metals showed no significant differences in the means of all elements and explained the close CV values of most elements (Table 2). Observed results could be attributable to the effectiveness of the 2 methods in elemental analysis as McBride,⁵ Gorecka et al,¹⁷ and Paya-perez et al¹⁹ reported in comparative analyses of trace elements in wood ashes, soil extracts, and sediments, respectively.

Linear regression analysis

Results showing comparison of the 2 methods using linear regression are presented in Figures 4 to 7. V, Cr, Co, Ni, Cu, Zn, Sr, and Pb had almost ideal linear ($y=x$) relationships with R^2 values of 0.9999, 0.9997, 0.9831, 0.939, 0.9327, 0.9998, 0.9867, and 0.9992, respectively. The results confirmed a definitive agreement in concentrations obtained from the 2 methods and confirmed their reasonable recoveries and yields in metal

analyses as Han et al²⁶ who analyzed both plants and soils from Starkville plains of Mississippi (USA) using the 2 methods suggested. Similarly, a metal analysis in oysters by Sneddon and Vincent¹⁸ reported high agreement of concentrations from the 2 techniques. Paya-Perez et al¹⁹ recommended the methods as fast and have good precision and reproducibility in a comparative study using contaminated soils from Aberdeen, UK.

Ca, Mg, Ti, Fe, and Mn concentrations showed high agreement with R^2 values of 0.8069, 0.8967, 0.8593, 0.8873, and 0.8907, respectively. Although there was a high degree of agreement, their regression lines showed some deviations and substantial scatter despite the fact that similar soil digestants were used to overcome errors of subsample heterogeneity. Overall, all quantified metal concentrations did not exhibit extreme deviations from the correlation line. This observation pointed to interferences and inherent errors of ICP-OES and ICP-MS spectrometric techniques as the causes of observed deviations. A study by McBride⁵ that assessed the levels of Cd in agricultural soils of New York (USA) reported bias after regressing concentrations of the 2 methods and attributed it to systematic errors, elemental and matrix interferences.

Sneddon and Vincent¹⁸ confirmed that spectral interferences lower concentrations by inducing elemental adsorption and co-precipitation in quantifiable samples. Velitchkova et al¹³ added that quantifying Mg, Ca, Ti, and Fe using ICP-OES is

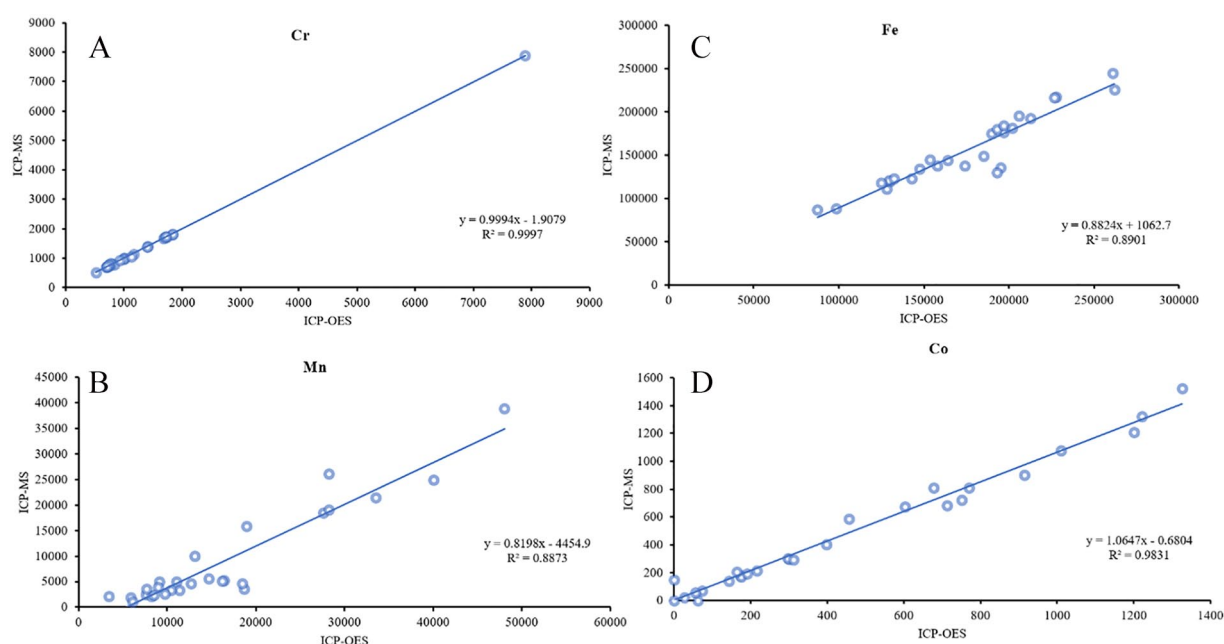


Figure 5. Regression results for ICP-MS and ICP-OES for (A) Cr, (B) Mn (C) Fe, and (D) Co. ICP-MS indicates inductively coupled plasma mass spectrometry; ICP-OES, inductively coupled plasma optical emission spectrometry.

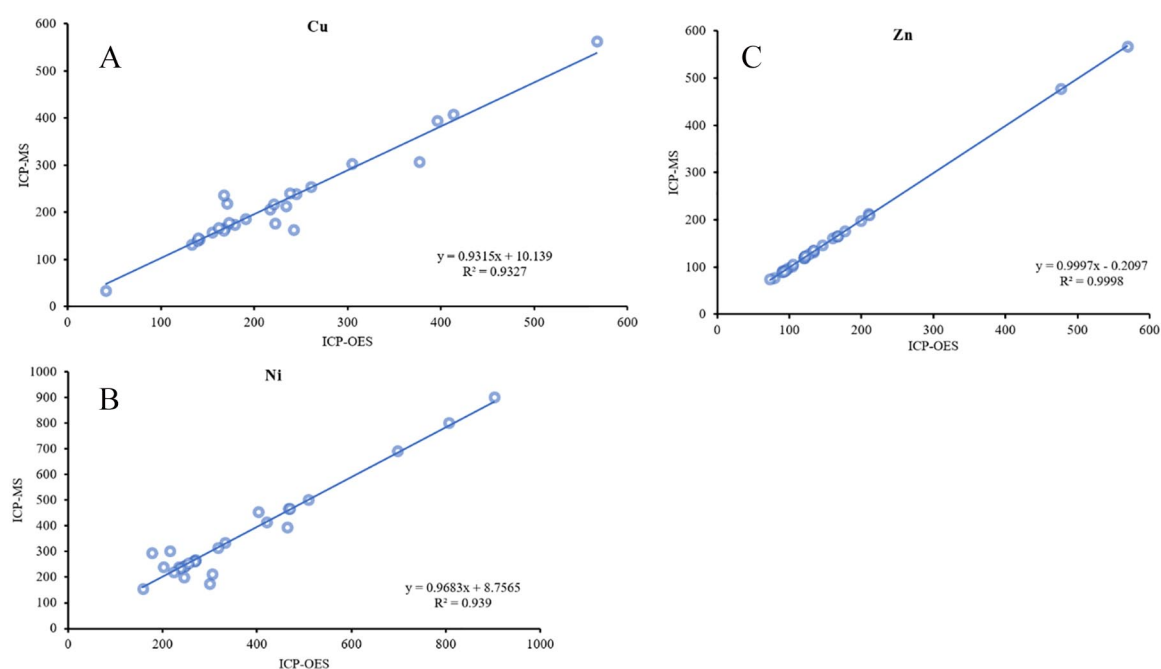


Figure 6. Regression results for ICP-MS and ICP-OES for (A) Cu, (B) Ni, and (C) Zn. ICP-MS indicates inductively coupled plasma mass spectrometry; ICP-OES, inductively coupled plasma optical emission spectrometry.

vulnerable to overlap interferences arising from spectrum background enhancement and influences the accuracy of trace elements. Bias in the 2 methods could also be a result of acid matrix interference when preparing reference and blank solutions and line interferences considering that the analysis was multi-elemental. Such interferences lead to inaccuracies in concentration and detection limits determination of trace metals as they affect their hydroxide and oxide ions leading to

cohesion.^{29,30} Helaluddin et al²⁵ attributed these biases in quantifying metal elements using the 2 methods to spectral chemical and sample throughput interferences that lead to sample precipitation and are more pronounced in ICP-OES compared with ICP-MS.

The accuracy of determining rare trace elements (V, Cr, Pb) using the 2 methods is higher compared with common metal elements (Mg, Ca, Ti, Fe, and Mn). This could be attributable to the

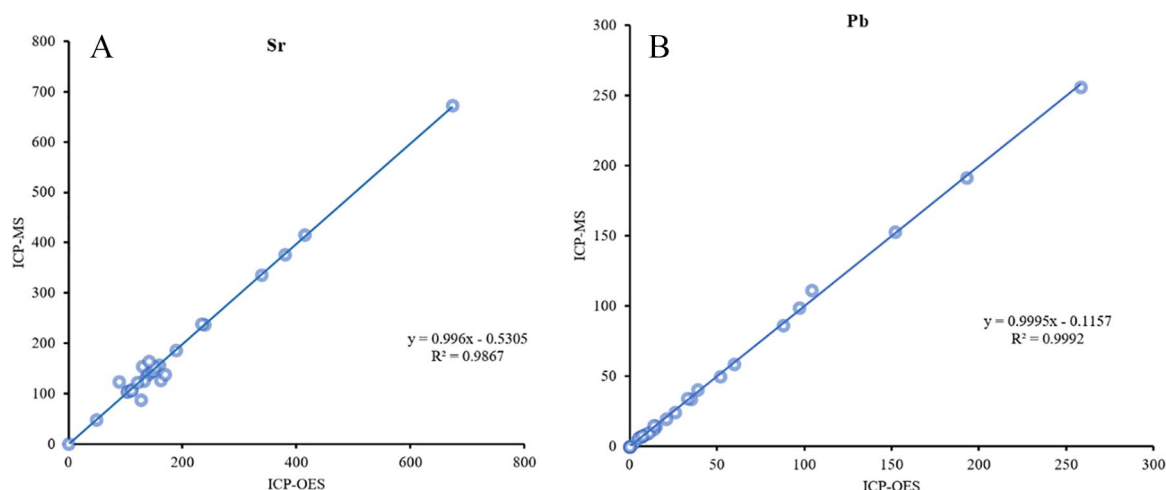


Figure 7. Regression results for ICP-MS and ICP-OES for (A) Sr and (B) Pb. ICP-MS indicates inductively coupled plasma mass spectrometry; ICP-OES, inductively coupled plasma optical emission spectrometry.

limitations in both techniques whereby ICP-MS is highly sensitive with detection limits of parts per trillion (ppt) and hence requires sample dilution to prevent multiplicative interferences, whereas ICP-OES has detection limits of ppb and dilution is not compulsory.¹⁸ The use of similar samples for uniformity in the 2 methods could have induced multiplicative interferences for ICP-MS, hence the observed bias. Detection limits of the 2 methods could explain the high linearity for the rare trace elements that were within the ppb-ppt range compared with major elements such as Fe, Mn, and Ti whose concentrations in the case of ICP-MS quantification were high. Ammerman et al³¹ also agreed with these suggestions claiming that ICP-MS is highly sensitive to trace elements and may not be suited for major elements such as Mg, Al, Ca, and Fe found in high concentrations in soils unlike ICP-OES, unless sample dilution is done prior to analysis. Bias in the 2 methods could also be a result of memory and carry-over effects where some elements adhere on the spray chamber wall and in the sample introduction system during analysis deterring reproducible and accurate analysis. In a soil and plant metals by Han et al²⁶ using ICP-OES, these effects reduced Hg concentrations unless standards, blanks, and samples were spiked with gold to preserve the element in solution form. The complex nature of soils particularly the presence of polyatomic anions and halides, which induce formation of poorly soluble oxides and hydroxides by metals, was blamed for biased ICP-MS analysis characterized by metal chelation, concentration underestimation, and memory effects.³²

This study demonstrates the possibilities that ICP-MS and ICP-OES offer in elemental analysis research work. Although there was ideal agreement in correlation plots of the 2 methods, ICP-MS was the superior method owing to its precision, high sensitivity, and ability to reduce poly-elemental spectral interference through peak hopping. A comparative trace element analysis in water samples from Swarzedzkie region of Poland found the method to have better precision compared with ICP-OES.³³ A soil analysis in New York state reported that ICP-MS is highly sensitive to Cd at near background

levels compared with ICP-OES that is vulnerable to spectral interferences.⁵ The ability of ICP-MS to reach lower limits of quantification in V and Ni assessment from crude oil in Chevron, California, confirmed its superiority compared with ICP-OES.³⁴

Conclusions

This study confirmed that spectrometric techniques are effective tools for metal analysis in complex matrices such as soils. Reproducibility of ICP-OES and ICP-MS for V, Cr, Co, Ni, Cu, Zn, Sr, and Pb analysis was definitive compared with Mn, Ti, Ca, Fe, and Mg that was high but showed deviations in their regression lines. The multi-element nature of soils characterized by chelation of ions to form insoluble compounds was attributable to resultant analytical bias and errors. ICP-OES was vulnerable to systematic, spectral, and throughput interferences unlike ICP-MS that was prone to multiplicative and drift errors. Inherent equipment errors could have resulted to low sample uptake, poor recoveries, under- and overestimation of concentrations. Statistical analysis however did not show any significant differences in the mean concentrations obtained using the 2 methods for all elements. Specific strengths of each analytical technique can be adopted to ensure holistic and precise analysis of metals in complex matrices such as soils. High precision and sensitivity of ICP-MS proved that it is a superior technique compared with ICP-OES.

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Author Contributions

JN sampled soils, conducted the experiments and prepared the manuscript. EO supervised the sampling and experimental work and with the help of MOD and SBM reviewed the prepared manuscript.

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REFERENCES

1. Stacey PR. The performance of laboratories analysing heavy metals in the workplace analysis scheme for proficiency. *Ann Occup Hyg.* 2006;1:417-425.
2. Paul AP, Garbarino JR, Olsen LD, Rosen MR, Mebane CA, Struzeski TM. Potential sources of analytical bias and error in selected trace-element data quality analyses (U.S. Geological Survey Scientific Investigations Report 2016-5135). <https://pubs.usgs.gov/sir/2016/5135/sir20165135.pdf>. Updated 2016.
3. Betz JM, Brown PN, Roman MC. Accuracy, precision and reliability of chemical measurements in natural products research. *Fitoterapia.* 2011;82:44-52.
4. Masson P, Dalix T, Bussiere S. Determination of major and trace elements in plant samples by inductively coupled plasma-mass spectrometry. *Commun Soil Sci Plan.* 2010;41:231-243.
5. McBride M. A comparison of reliability of soil cadmium determination by standard spectrometric methods. *J Environ Qual.* 2011;40:1863-1869.
6. Pontes MJ, Cortez J, Galvão RK, et al. Classification of Brazilian soils by using LIBS and variable selection in the wavelet domain. *Anal Chim Acta.* 2009;642:12-18.
7. Yi R, Guo L, Zou X, et al. Background removal in soil analysis using laser-induced breakdown spectroscopy combined with standard addition method. *Opt Express.* 2016;24:2607-2618.
8. Essington ME, Melnichenko GV, Stewart MA, Hull RA. Soil metals analysis using laser-induced breakdown spectroscopy (LIBS). *Soil Sci Soc Am J.* 2009;73:1469-1478.
9. Woodard T, Amarasiwardena D, Shrout K, Xing B. Roadside accumulation of heavy metals in soils in Franklin County, Massachusetts, and surrounding towns. *Commun Soil Sci Plan.* 2007;38:1087-1104.
10. Taylor H. *Inductively Coupled Plasma-Mass Spectrometry, Practices and Techniques.* New York, NY: Academic Press; 2001.
11. Murphy K, Vetter T. Recognizing and overcoming analytical error in the use of ICP-MS for the determination of cadmium in breakfast cereal and dietary supplements. *Anal Bioanal Chem.* 2013;405:4579-4588.
12. Hoenig M. Preparation steps in environmental trace element analysis, facts and traps. *Talanta.* 2001;54:1021-1038.
13. Velitchkova N, Pentcheva EN, Daskalova N. Determination of arsenic, mercury, selenium, thallium, tin and bismuth in environmental materials by inductively coupled plasma emission spectrometry. *Spectrochimica Acta Part B.* 2004;59:871-882.
14. Moor C, Lymberopoulou T, Dietrich VJ. Determination of heavy metals in soils, sediments and geological materials by ICP-OES and ICP-MS. *Mikrochimica Acta.* 2001;136:123-128.
15. Franklin R, Duis L, Smith B, Brown R, Toler J. Elemental concentrations in soils of South Carolina. *Soil Sci.* 2003;168:280-291.
16. Hickman D, Maclean S, Shepley D, Shah R. *Inductively Coupled Plasma Mass Spectrometry Uranium Error Propagation.* Berkeley, CA: University of California; 2001.
17. Gorecka H, Chojnacka K, Gorecki H. The application of ICP-MS and ICP-OES in determination of micronutrients in wood ashes used as soil conditioners. *Talanta.* 2006;70:950-956.
18. Sneddon J, Vincent MD. ICP-OES and ICP-MS for the determination of metals: application to oysters. *Anal Lett.* 2008;41:1291-1303.
19. Paya-Perez A, Sala J, Mousty F. Comparison of ICP-OES and ICP-MS for the analysis of trace elements in soil extracts. *Int J Environ An Ch.* 2006;51:223-230.
20. Kalule K. A case study for developing a framework for ecological risk assessment for landfill sites in South Africa. *J Environ Qual.* 2015;21:102-115.
21. Dookhi N, Jewskiewitz S, Jewskiewitz B. East London Regional (Roundhill) waste disposal site: wasting no time on the road to compliance. *J S Afr Inst Civ Eng.* 2015;23:35-41.
22. Element C. *Method 3015A: Microwave Assisted Acid Digestion of Aqueous Samples and Extracts.* Washington, DC: Environmental Protection Agency; 2007.
23. Ahmed A, Abdullah P, Khalikwood A, Hamza S, Othman M. Determination of some trace elements in marine sediment using ICP-MS and XRF: a comparative study. *Orient J Chem.* 2013;29:645-653.
24. Maliki A, Al-lami A, Hussain H, Al-Ansari N. Comparison between inductively coupled plasma and X-ray fluorescence performance for Pb analysis in environmental soil samples. *Environ Earth Sci.* 2017;76:433.
25. Helaluddin A, Khalid RS, Alaama M, Abbas S. Main analytical techniques used for elemental analysis in various matrices. *Trop J Pharm Res.* 2016;15:427-434.
26. Han F, Patterson D, Xia Y, Sridhar M, Su Y. Rapid determination of mercury in plant and soil samples using inductively coupled plasma atomic emission spectroscopy: a comparative study. *Water Air Soil Poll.* 2006;170:161-171.
27. Nardi E, Evangelista F, Tormen L, et al. The use of inductively coupled plasma mass spectrometry (ICP-MS) for the determination of toxic and essential elements in different types of food samples. *Food Chem.* 2009;112:727-732.
28. Zhao K, Fu W, Ye Z, Zhang C. Contamination and spatial variation of heavy metals in soil-rice system in Nanxun county, Southeastern China. *Int J Env Res Pub He.* 2015;12:1577-1594.
29. Boevski N, Havezov I. Determination of barium, chromium, cadmium, manganese, lead and zinc in atmospheric particulate matter by inductively coupled plasma atomic emission spectrometry (ICP-OES). *Spectrochim Acta B.* 2000;55:1643-1657.
30. Guo S. Direct determination of trace cadmium in environmental samples by dynamic reaction cell inductively coupled plasma mass spectrometry. *Chemosphere.* 2010;81:1463-1468.
31. Ammerman J, Huang C, Sailstad J, et al. Technical aspects of inductively coupled plasma bioanalysis techniques. *Bioanalysis.* 2013;5:1831-1841.
32. Pappas SR. Sample preparation problem solving for inductively coupled plasma-mass spectrometry with liquid introduction system I. Solubility, chelation, and memory effects. *Spectroscopy.* 2012;27:20-31.
33. Baralkiewicz A, Gramowska H, Hanc A, Krzyzaniak I. A comparison of ICP-OES and ICP-MS in the determination of elements in lake water. *Atom Spectrosc.* 2007;28:164-170.
34. Poirier L, Nelson J, Leong D, Berhane L, Hajdu P, Lopez-Linares F. Application of ICP-MS and ICP-OES on the determination of nickel, vanadium, iron and calcium in petroleum crude oils via direct dilution. *Energy Fuel.* 2016;30:3783-3790.