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Determination of trace elements in mine soil samples using a portable X-ray fluorescence spectrometer: A comparative study with ICP-OES

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Abstract

Lead (Pb), zinc (Zn) and cadmium (Cd) levels in soils surrounding Lakhouat mine (Northwest Tunisia) were measured. The total concentration of these elements in the soil samples was determined using portable X ray fluorescence (XRF) in situ and compared to the traditional digestion method using inductively coupled-plasma optical emission spectroscopy (ICP-OES). Statistical analyses were performed to determine significant differences between the instrumental techniques, which included simple regression correlations and t-tests of mean values for comparison. The statistical analysis demonstrated that no statistically significant differences were observed for the Pb determinations. However, for the Zn and Cd concentrations, t tests showed significant differences between the instrumental techniques. Application of the XRF method provides the possibility of rapid multi element soil analyses.

Keywords: Trace elements, Mine soils, ICP-OES, Portable XRF, In situ analysis

1. Introduction

Ore extraction and processing generate large quantities of metal-contaminated wastes which release trace elements over a longer duration even after the cessation of mining activity. Trace elements present in tailings can contaminate surrounding soils mediated by erosion, weathering and leaching [1-2]. Therefore, determination of total concentration of trace elements on soils surrounding mining area constitute a widely method to quantify the spatial distribution of these elements [3-4].

The accurate determination of trace elements content in soil samples is of primary importance and it still represents a significant challenge. Taking in account the complexity of the matrices involved, the identification of reliable and fast methods for this application is a difficult goal to achieve.

Atomic absorption spectroscopy (AAS) and inductively coupled plasma-optical emission spectroscopy (ICP-OES) has been the Soil Science laboratories methods of choice for the elemental analysis of soil extracts because of their utility, sensitivity, and reliability. These methods can rapidly determine trace elements contents, after digestion, in many types of contaminated soils with very low detection limits for most elements. These methods are well characterized and widely used, often for establishing analytical reference values for site samples. These traditional analytical methods require pre-treatment process of soil samples with acid digestion. This step is the time consuming process and easily causes the inputs of cross contamination among samples [5]. On the other hand, in the course of initiating a hazardous site remediation, portable X-ray fluorescence (XRF), were evaluated for site characterization as alternative method ICP-OES. XRF spectroscopy is considered as efficient field-portable technique for environmental screening, and provides rapid, multi-element measurements with minimal sample preparation [6-7].

Furthermore, portable XRF is a very sensitive nondestructive method for analyzing the content of various chemical elements in soils. XRF can analyze some 15–30 elements with atomic numbers ranging from Z= 11 to Z= 41 and some of the rare earth elements [8-9]. For more reliability, it is better to chemically isolate or pre-concentrate the elements of interest to minimize or eliminate matrix effects and interferences. Its biggest advantage is the availability of tubes as well as radionuclides as exciting sources.

In XRF analysis, a representative sample is exposed to an energetic beam of photons and the generated characteristic X rays are measured in order to arrive at the concentrations of the elements present in the sample.

The objectives of this study was to compare a portable XRF analyzer with the traditional analytical methods, ICP-OES on soils surrounding Lakhouat mine and to present some advantages for using portable XRF over ICP-OES.

2. Materials and methods

The study area is situated on Lakhouat mining area (North West of Tunisia, UTM Zone 32 North 522005.378/ 4014334.773). Seven samples (S1 to S7) were randomly collected to a depth of 30 cm and stored in polyethylene bags. An XRF portable (Bruker, S1 TITAN) with a 50 kV Rh

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anode X-ray tube in situ was used for determining total Pb, Zn and Cd levels soils from the mining area. Any plants growth and foreign objects were removed from the place of sampling so that the analyzer probe is flush to the surface soil. In situ analyzing of mine soil was determined by placing XRF portable directly onto the soils surface. Screening analysis involved taking several 2 minutes surface XRF readings.

For ICP-OES analysis, the same samples were air dried at ambient temperature, passed through a 2-mm sieve and homogenized in a vibratory homogeniser for solid samples. Then, total trace element content was extracted by means of acid digestion using a mixture of concentrated nitric, hydrochloric and hydrofluoric acids (1:3:3 v/v/v) in Teflon bombs placed in a hot plate with 5g of each soil sample. Trace element analysis was carried out by ICP-OES, Perkin Elmer Optima 4300DV [10].

Variances and means between ICP-OES and XRF methods were calculated with the paired-data test with the Pb, Zn and Cd results using the software SPSS® for Windows version 20.0.

3. Results and discussion

3.1. Comparison of the performance of portable XRF/ICP-OES analytical techniques

A comparison between XRF and ICP-OES analytical techniques was performed using statistical tools. Paired-data test was calculated for the data of both methods, with a confidence interval of 95% assuming the same null and alternate hypothesis for *t*-tests performed on the mine soil samples.

Figures 1, 2 and 3 show the results obtained by the two instrumental methods using regression line. Each point represents the average of several repetitions. The straight line represents the hypothetical overlap of the results of the two methods.

In general, a decreasing trend on Pb, Zn and Cd concentrations in mine soil samples was showed for both instrumental techniques (Tables 1, 2 and 3).

Concerning Pb, the current set of surface mine soil samples contained the total ePb in the range of 285–1800ppm for XRF and 692–2925 for ICP-OES (Table 1). Most of the reported data showed strong deviation between ICP-OES and XRF results with R^2= 80% at 5% significant level (Figure 1).

On the other hand, Zn concentrations were in the range of 839–25127 ppm for XRF and 2327–7629 for ICP-OES (Table 2), whereas Cd concentrations were ranged from 18–219 ppm for XRF and 13–39 for ICP-OES (Table 3). Regression analysis showed that these two elements exhibited less agreement than Pb with 68% and 77%, respectively (Figure 2 and 3). In addition we noticed also, for the three studied elements that low concentrations had a relatively high correlations between XRF and ICP-OES analysis.

Under the assumption that the variances of both instrumental methods are not independent, a new paired-data testing is calculated to determine if the means from the two methods are the same.

The paired-data test (Table 4) for Zn and Cd showed a disparity between the values obtained from the different analytical methods. This result demonstrates that variances from both instrumental techniques were statistically different (significance >0.05).

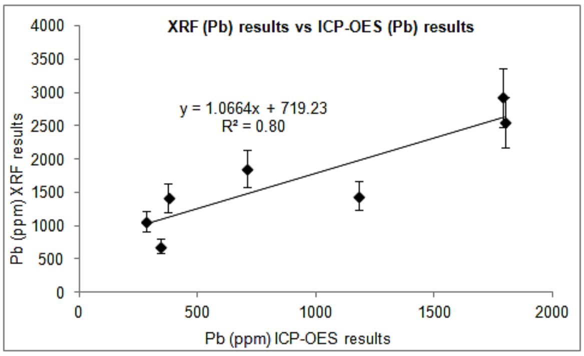

Figure 1 Correlation diagram. Pb concentration data obtained with XRF *vs* those obtained by ICP-OES.

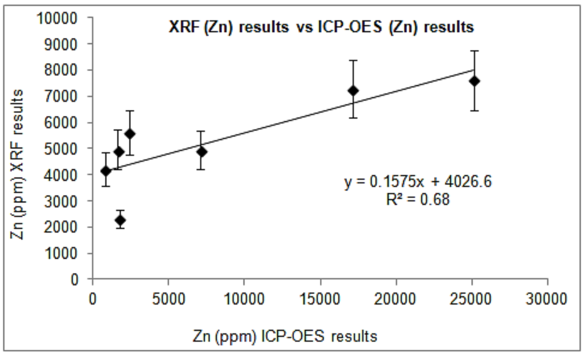

Figure 2 Correlation diagram. Zn concentration data obtained with XRF *vs* those obtained by ICP-OES.

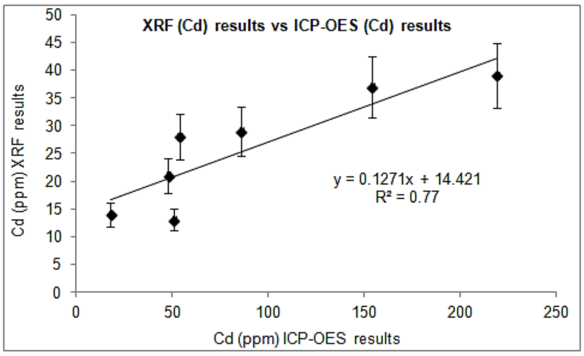

Figure 3 Correlation diagram. Cd concentration data obtained with XRF *vs* those obtained by ICP-OES.

Table 1 Mean values of Pb concentration in mine soil samples (n=3). Comparative results obtained using the XRF and ICP-OES

Sample	Pb (ppm) by XRF	Pb (ppm) by ICP-OES
S1	1800	2549
S2	1789	2925
S3	709	1852
S4	377	1420
S5	285	1065
S6	344	692
S7	1181	1447

Table 2 Mean values of Zn concentration in mine soil samples (n=3). Comparative results obtained using the XRF and ICP-OES

Sample	Zn (ppm) by XRF	Zn (ppm) by ICP-OES
S1	17110	7297
S2	25127	7629
S3	2365	5624
S4	1636	4966
S5	839	4220
S6	1757	2327
S7	7107	4935

Table 3 Mean values of Cd concentration in mine soil samples (n=3). Comparative results obtained using the XRF and ICP-OES

Sample	Cd (ppm) by XRF	Cd (ppm) by ICP-OES
S1	219	39
S2	154	37
S3	86	29
S4	54	28
S5	48	21
S6	51	13
S7	18	14

In the opposite case, paired-data test (Table 4) showed that both XRF and ICP-OES methods are significantly different for Pb, proving that both methods have the same variances and means. These results show that the XRF technique is a good choice for Pb measurements in soil.

Similar results, on different contaminated soils, were obtained by several researchers. For example, Binstock et al. [11] analyzed Pb contaminated soils from six cities across the United States and showed a near 1:1 correspondence between mean portable XRF and ICP-OES soil Pb measurements. On the same way, comparison of Zn levels results obtained on soil samples from an old landfill site by ICP-OES and XRF analysis showed that the results are broadly in agreement and noted that either technique produced the same conclusion about the nature and extent of the contamination by Zn of the site [12]. Also, Ahmed et al. [13] by determining the total concentration of trace elements on sediment indicated that the two detection techniques agree with each other on Cd concentrations.

From these results we notice that XRF provides a good quality data for screening Pb, Zn and Cd in mine soils from low to high concentrations since most of these elements are present near the detection limits.

3.2. Advantages of utilizing portable XRF over ICP method

The current comparative study demonstrates that portable XRF analysis results were in general in much agreement with ICP-OES analysis results. For this reason, XRF can be recommended as a tool for trace elements spatial distribution studies on fields. As contrary to ICP-OES, XRF analyzer is characterized by advantages: 1) the limited preparation required for soil samples (Sample times for XRF in situ are typically less than 2 minutes), 2) non-destructive analysis, 3) increased total speed and high throughout, 4) the decreased production of hazardous waste and 5) Little to no sample preparation is required which greatly reduces the analysis time and cost, 6) multi-elemental determination and 7) portability in the fields.

The current comparative study demonstrates that XRF is a good rapid non-destructive method for trace elements contaminated mine soils. However, in terms of the range of elements that can be detected, ICP-OES has advantage over XRF since it has lower detection limit for most elements.

4. Conclusion

A field portable XRF analyzer was demonstrated to be capable of measuring Pb, Zn and Cd in soil samples collected from Lakhouat mine (Tunisia) and thus would be useful in contamination assessment of mining activities. Results from the Pb, Zn and Cd analysis by the field portable XRF were compared to results from the same samples analyzed ICP-OES. Correlations were excellent for Pb with R^2 values of 0.80 and lower for Zn and Cd with R^2 values of 0.68 and 0.77 respectively.

The comparison of XRF and ICP-OES analytical techniques with paired t-test showed no significant statistical difference in the analysis of Pb. However, Zn and Cd determinations showed that ICP-OES and XRF had significant differences between the concentrations determined by each instrumental technique.

Portable XRF instruments can perform well in environmental surveys for trace elements pollution in large contaminated areas (mining sites, wastewater irrigated soils, industrial areas…). Portable XRF can also diagnostic the contaminated areas and thus help to making decision regarding which contaminated areas should be dealt with first.

Table 4 Paired-data test between the results of ICP-OES and portable XRF analysis for Pb, Zn and Cd

	Paired Differences						
				95% Confidence Interval of the Difference			
(XRF Analysis) - (ICP-OES)	Mean	Std.Dev.	Std. Error Mean	Lower	Upper	t	Sig. (2-tailed)
Pb	926.43 1800.26	360.42	136.22	-1114.05	-447.37	-5.73	0.001
Zn	7991.57 5044.00	8056.01	3044.88	-4744.42	10156.71	0.89	0.408
Cd	90.00 26.86	62.45	23.60	6.38	121.90	2.72	0.035

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