

Determination of Cu, Zn, Mn & Fe Metals in Soil Employing the EDXRF & FAAS Techniques and Comparative Study of Results

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Abstract Two analytical spectroscopic techniques *viz.* EDXRF and FAAS were employed in analyzing the four heavy metals i.e. Cu, Zn, Mn and Fe in 24 soil samples. The heavy metals in understudy soil were found to have very low to high concentration range and so both techniques were compared for a broader range of concentrations. Two methods, open vessel digestion and microwave oven digestion, were used to prepare the liquid samples for FAAS analysis. The results of both of the EDXRF and FAAS techniques were found comparable when high concentration element Fe was determined. However, for the low concentration values, the results were dissimilar. Some statistical methods like regression and Levene's test are used to compare the results of both the techniques.

Keywords: EDXRF, FAAS, Linear Regression, Levene's Test

1. INTRODUCTION

Analytical spectroscopic techniques have a wide range of application to characterize different kind of materials. Many techniques are in use to find the elemental profile or concentrations in various kinds of samples. Two most promising and widely used workhorse are Energy Dispersive X-Ray Fluorescence (EDXRF) and Atomic Absorption Spectroscopy (AAS). In the

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current study, both the techniques are used in studying soil samples. Soil is a complex, unconsolidated mixture of inorganic, organic and living material and both the techniques can be well examined in characterizing the soil.

The EDXRF technique is widely used for the multi-element source profile of different environmental matrices. Soils and other materials have been analyzed by EDXRF probe to determine the concentrations of trace elements, heavy metals and other elements in different matrices [6,7, 14-17, 19-20]. In most studies, the emphasis has been given on the determination of heavy metals in soils [13, 4].

Flame atomic absorption spectrometry (FAAS) is a mature analytical method for elemental determinations of elemental metals. Aqueous samples can be generally introduced for analysis directly and without any prior treatment but the solid samples are usually analyzed by dissolving the sample to form a liquid solution that can be introduced into the flame. Dissolution can be accomplished by mineral acid digestion (wet ashing) that involves the utilization of mineral or oxidizing acids and an external heat source to decompose the sample matrix [1]. FAAS technique has been employed in soil studies, particularly for heavy metals assessment [10, 8, 5, 12].

In the current study, the concentrations of four metals i.e. Cu, Zn, Me and Fe were determined in soil samples using both FAAS and EDXRF methods and the results were compared. These four selected metals were found to have very low value of concentration for Cu to a high value for Fe, and this was the basis of selection of mentioned heavy metals as the results of both techniques would be compared for different concentration levels. EDXRF set-up was calibrated using the empirical calibration approach. Two methods, open vessel acid digestion and microwave acid digestion, were used to prepare the samples for FAAS analysis. Further, the results were investigated using the Levene's test. It tests the null hypothesis that the population variances are equal and if the null hypothesis of equal variances is rejected, it is concluded that there is a difference between the variances in the population.

2. MATERIAL AND METHODS

2.1 Soil sampling sites

The soil samples were collected from an on trial agricultural field of the Crop Research Centre (CRC), G.B. Pant University, Pantnagar. A number of 24 samples, subjected to various fertilizers treatments, were collected. Three replicates were used for each EDXRF analysis. The soil of this particular region is classified subgroup-Aquic hapludoll, Family-Fine Loamy and series-Silty Clay Loam.

2.2 Sample preparation for EDXRF analysis

There are several methods for solid samples preparation, including fusion, powder samples etc., but we used pellet samples to be analyzed by EDXRF. The sample prepared in the form of pellets has the advantage of high X-ray intensity. The samples were air-dried, homogenized and sieved properly before making the pellets for EDXRF. Two hundred mg of samples were taken to make the pellets and a press pelletizer has been used to make the 13 mm diameter pellets, applying a pressure of 150 kg/cm².

2.3 EDXRF set-up details

A Jordan Valley EX-3600 EDXRF spectrometer with the Si(Li) detector resolution of 143 eV at 5.9 keV photo peak was used to obtain the elemental profile of concern soil. The detection limit of the set-up for the elements on the periodic table between atomic numbers 11 (Na) and 92 (U) is 5-10 ppm. The empirical calibration technique was employed using Standard Reference Material (SRM) 1646a. The built-in ExWin software was used for the quantitative analysis. To optimize the EDXRF sensitivities, different combinations of EDXRF parameters were employed [16]. The X-ray filters were used to eliminate the noise.

2.4 Sample preparation for FAAS analysis

Two methods were used to prepare the liquid solution of understudy soil samples, for the FAAS analysis.

Method 1: Open vessel dissolution of soil using HNO₃, HF and HClO₄

Method of sample preparation was adopted after the work of Kratochvil and Mamba (1990). A 500-mg of fine soil was placed in a digestion vessel and 6 mL HNO₃, 3 mL HF, and 2 mL HClO₄ were added. The vessel was capped and placed in boiling water for 2.5 h. After cooling, the contents were fumed to near dryness at 200 °C. The obtained residue was dissolved in 2 mL HNO₃ and 2 mL HClO₄ and fumed again to near dryness. The colorless residue was dissolved again in 2 mL HNO₃ and a clear solution was obtained which again diluted to 100 mL in high pure water. In prepared samples, the total elemental concentrations of elements Cu, Fe, Mn and Zn were determined by FAAS.

Method 2: Closed vessel microwave acid digestion using HNO₃ and HF

A procedure of [2] was adopted to prepare the samples. 250 mg of soil was combined with 9.0 mL HNO₃, 4.0 mL HF and 1.0 mL of de-ionized water in a digestion vessel and the lids tightened with a plastic wrench. The samples were

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heated for 15 min at 1,200 W. After cooling the sample, the solutions were diluted to 25 ml with 1% HNO₃ and stored. The total elemental concentrations were determined in the samples by FAAS.

Prior to the AAS analysis, the calibration of the set-up was achieved using standard solutions of understudy elements.

3. RESULT AND DISCUSSION

3.1 Elemental analysis of soil

Four elements Mn, Fe, Cu and Zn were determined in 24 soil samples employing two techniques *viz* FAAS and EDXRF (Fig. 1) and the results were compared. Two digestion methods have been employed for AAS analysis of soil samples and the concentrations of metals found by AAS were higher than EDXRF in all the samples. The FAAS results, obtained using microwave acid dissolution procedure were nearer to conventional dissolution. The maximum and minimum concentration values with standard deviation for four heavy metals, determined by FAAS and EDXRF, are presented Table 1. In almost all samples, the concentrations values of four understudy heavy metals were obtained maximum when the samples, prepared by open vessel dissolution method, were characterized with FAAS. EDXRF results have shown lower concentrations of understudy heavy metals compared to FAAS results.

The mean values, obtained for Cu element, were 8.16, 14.82 and 14.16 for EDXRF, FAAS open vessel method and FAAS microwave digestion techniques, respectively. Clearly, results suggest that both the EDXRF and FAAS technique outcomes are dissimilar when the elements having low

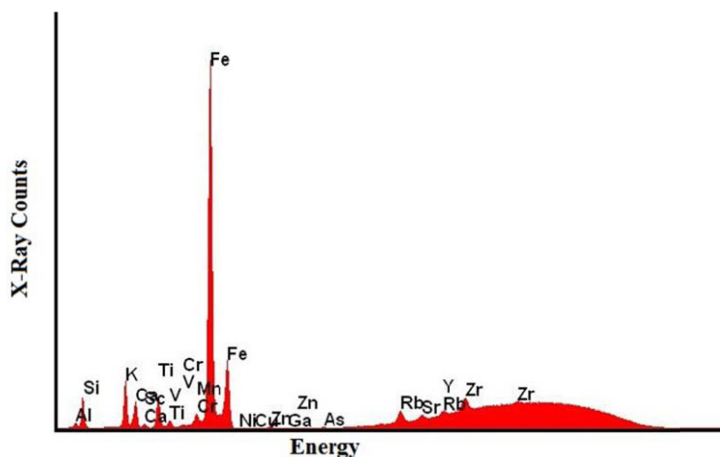


Figure 1: The EDXRF spectrum of a soil sample.

Table 1: Statistical data of concentrations of metals Cu, Zn, Mn and Fe determined by EDXRF and FAAS (All values are in ppm unit).

Element	Characterization Technique								
	EDXRF			AAS*			AAS**		
	Max	Min	Std. Dev(±)	Max	Min	Std. Dev(±)	Max	Min	Std. Dev(±)
Cu	9.34	6.3	0.8	17.83	9.89	2.0	17.23	10.12	1.8
Zn	48.36	36.99	2.8	68.98	46.88	5.8	66.29	45.9	5.5
Mn	563.39	441.51	25.3	662.88	500.09	40.4	635.01	461.67	38.8
Fe	68542.35	53385.35	3558.2	74581.38	56852.55	4087.8	72089.98	55347.24	3775.2

*Open vessel digestion, **Microwave oven digestion

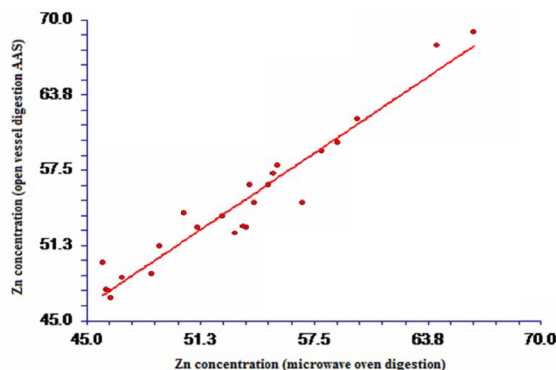


Figure 2: The highest correlation ($r^2 = 0.935$) was observed between AAS (microwave oven digestion) and AAS (open vessel digestion) techniques in determining Zn concentration in soil samples.

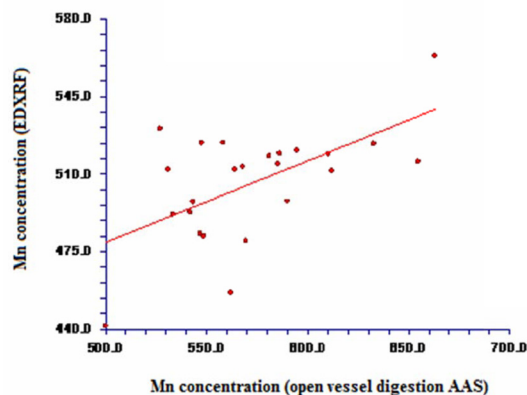


Figure 3: The lowest correlation ($r^2 = 0.343$) was observed between EDXRF and AAS (open vessel digestion) techniques in determining Mn concentration in soil samples.

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Table 2: Linear regression relation among results of EDXRF, open vessel digestion AAS and microwave oven digestion.

Element	Equation	r ²
Mn	$\text{ppmMn(EDXRF)} = 0.368 \text{ ppmMn(AAS}^*) + 295.085$	0.343
	$\text{ppmMn(EDXRF)} = 0.404 \text{ ppmMn(AAS}^{**}) + 284.375$	0.381
	$\text{ppmMn(AAS}^*) = 0.885 \text{ ppmMn(AAS}^{**}) + 87.179$	0.723
Fe	$\text{ppmFe(EDXRF)} = 0.747 \text{ ppmFe(AAS}^*) + 12197.428$	0.736
	$\text{ppmFe(EDXRF)} = 0.791 \text{ ppmFe(AAS}^{**}) + 10370.432$	0.704
	$\text{ppmFe(AAS}^*) = 1.003 \text{ ppmFe(AAS}^{**}) + 1098.184$	0.857
Cu	$\text{ppmCu(EDXRF)} = 0.324 \text{ ppmCu(AAS}^*) + 3.356$	0.669
	$\text{ppmCu(EDXRF)} = 0.340 \text{ ppmCu(AAS}^{**}) + 3.344$	0.624
	$\text{ppmCu(AAS}^*) = 1.043 \text{ ppmCu(AAS}^{**}) + 5.069$	0.923
Zn	$\text{ppmZn(EDXRF)} = 0.458 \text{ ppmZn(AAS}^*) + 16.881$	0.876
	$\text{ppmZn(EDXRF)} = 0.483 \text{ ppmZn(AAS}^{**}) + 16.131$	0.885
	$\text{ppmZn(AAS}^*) = 1.015 \text{ ppmZn(AAS}^{**}) + 0.531$	0.935

*Open vessel digestion, **Microwave oven digestion

concentration are analyzed in samples. However, when the concentration of elements like Fe, which has the high concentration value in samples, was determined, the results of both techniques were comparable. These outcomes are in agreement with the previous result of [11] which revealed that when concentrations were close to detection limits, the output results might lose the accuracy. However, in contrast to the results of Makinen et al., no large deviations were observed for low concentration EDXRF results. In another study, it was observed that for low concentration Cu values, the results of AAS were more near to certified value than EDXRF [3]. The results were further investigated using linear regression (Table 2). Highest correlations among techniques were observed in determination on Zn element (Fig. 2). The techniques were also very comparable in determining the Fe

Table 3: Results of Levene's Test.

Element	F*	F**	DF ^a 1	DF 2	p-value	alpha	Decision
Mn	2.09	3.13	2	69	0.131	0.05	Null hypothesis is accepted
Fe	0.008	3.13	2	69	0.992	0.05	Null hypothesis is accepted
Cu	7.84	3.13	2	69	0.001	0.05	Null hypothesis is rejected
Zn	3.562	3.13	2	69	0.034	0.05	Null hypothesis is rejected

*observed value **Critical value ^aDegree of freedom

element and have shown good correlations. The least values of r^2 were observed in Mn determination (Fig. 3). This suggests that for mid range concentration values for Mn element, both the EDXRF and FAAS techniques produce highly dissimilar results and did not show a better relation.

3.2 Levene's test

The variances among results were investigated using Levene's test. The test was used to examine the precision in results of EDXRF and FAAS techniques (Table 3).

According to the test results, variances are equal in case of Mn and Fe concentration determinations by the three methods. It indicates that for higher concentration determination, the differences in the results of both EDXRF and FAAS are similar although the Mn concentration values determined by both techniques may differ significantly. In the case of Cu, results show that at least one of the variances is different from another, although the risk to reject the null hypothesis while it is true is lower than 0.09%. So, the results are quite comparable in Cu determination also. In Zn determination, at least one of the variances is different from another, according to the result. The variances among the groups and hence the results of both techniques are dissimilar when low concentration elements are analyzed.

For the elements, having low concentrations in sample, the observed EDXRF and FAAS concentration values were quite different. However in multiplicative manner, good correlation was observed even when analyzing the low concentrations elements by both techniques. For a very high concentration values, both techniques had produced similar values results and with good correlation too. The advantage of using EDXRF over FAAS is that the sample preparation is far easy and less time consuming and also harmful acid contact, used in acid

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digestion, can be avoided. If the elements having low concentration in sample have to be analyzed, FAAS may be a better option as the detection limit is better.

REFERENCES

- [1] Bader, N. R. (2011). Sample preparation for flame atomic absorption spectroscopy: An overview. *RASAYAN J. Chem.*, **4**, 49–55.
- [2] Chen, W., Krage, N., Wu, L., Page, A. L., Chang, A. C. (2008). Fertilizer Applications and Trace Elements in Vegetable Production Soils of California. *Water, Air, Soil Pollut.*, **190**, 209–229.
- [3] Dharani, N., Onyari, J. M., Maina, D. M., Mavuti, K. M. (2007). The distribution of Cu and Pb levels in Soils and *Acacia xanthophloea* Benth. From Lake Nakuru National Park Kenya. *Bull. Environ. Contam. Toxicol.*, **79**, 172–177.
- [4] Dubey, V., Singh, D., Panday, A. (2014). Chemical Studies on Dumpsite Soils (with specific Focus on Cu (copper) Level) within Municipal Area of Sidhi Town, District Sidhi (M.P.) India *ORIENTAL J. CHEM.*, **30**, 2077–2079.
- [5] Garg, V. K., Yadav, P., Mor, S., Singh, B., Pulhani, V. (2014). Heavy metals bioconcentration from soil to vegetables and assessment of health risk caused by their ingestion. *Biol Trace Elem Res.*, **157**, 256–265.
- [6] Gupta, D., Chatterjee, J. M., Ghose, R., Mitra, A. K., Roy, S., Sarkar, M. (2011). Energy-dispersive X-ray fluorescence study of elemental uptake in cauliflower. *PRAMANA J. Phys.*, **76**, 345–349.
- [7] Kahraman, A., Kaynak, G., Gurler, O., Yalcin, S., Ozturk, S., Gundogdu, O. (2009). Investigation of environmental contamination in lichens of Gökçeada (Imbroz) Island in Turkey. *Radiation Measurements*, **44**, 199–202.
- [8] Kanmani, S., Gandhimathi, R. (2013). Assessment of heavy metal contamination in soil due to leachate migration from an open dumping site. *Appl Water Sci.*, **3**, 193–205.
- [9] Kratochvil, B., Mamba, S. (1990). Microwave acid dissolution of soil samples for elemental analysis. *Can. J. Chem.*, **68**, 360–362.
- [10] Liang, J., Chen, C., Song, X., Han, Y., Liang, Z. (2011). Assessment of Heavy Metal Pollution in Soil and Plants from Dunhua Sewage Irrigation Area. *Int. J. Electrochem. Sci.*, **6**, 5314–5324.
- [11] Makinen, E., Korhonen, M., Viskari, E., Haapamaki, S., Jarvinen, M., Lu, L. (2005). Comparison of XRF and FAAS methods in analysing Cca contaminated soils. *Water, Air, Soil Pollut.*, **171**, 95–110.
- [12] Moralejo, M. D., P., Acebal, S. G. (2014). The Transfer of Cu, Zn, Mn and Fe between Soils and Allium Plants (Garlic and Onion), and Tomato in the Southwest of the Buenos Aires Province, Argentina. *American J. Plant Sci.*, **5**, 480–487.
- [13] Popescu, I. V., Frontasyeva, M., Stihl, C., Cimpoia, G. V., Radulescu, C., State, G., Gheboianu, A., Oros, C., Culicov, O., Bancuta, I., Dulama, I. (2011). Atomic and nuclear methods applied in the study of heavy polluting elements. *Romanian Reports in Physics*, **63**, 1205–1214.
- [14] Rautray, T. R., Behera, B., Badapanda, T., Vijayan, V., Panigrahi, S. (2009). Trace element analysis of fly ash samples by EDXRF technique. *Indian J. Phys.*, **83**, 543–546.

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- [15] Saradhi, I. V., Sandeep, P., Pandit, G. G. (2014). Assessment of elemental contamination in road dust using EDXRF. *J. Radioanal. Nucl. Chem.*, **302**, 1377–1383.
- [16] Singh, V., & Agrawal, H. M. (2013). *Analytical Spectroscopy for Environmental Assessment*. Saarbrücken Germany: LAMBERT Academic Publishing, ISBN: 978-3-8473-2233-7.
- [17] Singh, V., Agrawal, H. M.^a (2012). EDXRF Analysis of Soil Samples to Study the Role of Trace Elements in Optimizing the Yield. *Int. J. Modern Engineering Res.*, **2**, 1454–1458.
- [18] Singh, V., Agrawal, H. M.^b (2012). Qualitative soil mineral analysis by EDXRF, XRD and AAS probes. *Radiat. Phys. Chem.*, **81**, 1796–1803.
- [19] Sudarshan, M., Ram, S. S., Majumdar, S., Maity, J. P., Ray, J. G., Chakraborty, A. (2011). Energy-dispersive X-ray fluorescence – A tool for interdisciplinary research. *PRAMANA J. Phys.*, **76**, 241–247.
- [20] Tiwari, M., Sahu, S. K., Bhangare, R. C., Ajmal, P. Y., Pandit, G. G. (2013). Depth profile of major and trace elements in estuarine core sediment using the EDXRF technique. *Appl. Radiat. Isot.*, **80**, 78–83.

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