

**COMPARATIVE ANALYSIS OF SOME DIGESTION METHODS USED IN THE
DETERMINATION OF METALS IN SOIL AND SEDIMENTS.**

ABSTRACT

Analytical study was carried in order to compare the accuracy of three (3) frequently used digestion methods, in the determination of metals in soil and sediments. Samples of soil and sediments were taken from three different location sites at Bakalchi, Batare, and Anguwan Honna in Girei Local Government Area in Adamawa State Nigeria. Sample matrix was formed from the three sample and the three methods was carried out on each of the sample matrix formed, the methods are methods I: Roast before digestion using aqua regia as used by Ehi (2012), Method II: Air dried and digest using Aqua-regia similar to the work of Saxena (1990), and Method III; Roast using ammonium chloride before digestion with aqua regia; (Voica C., et al 2010). The metal elements Calcium and Iron were chosen because of their relative abundance in natural soil and sediments. Results obtained show that the soil and sediments samples contain the metal element calcium and Iron which were used to examine, frequently used digestion methods. Based on the result obtained from the analysis, method III (Roast with NH_4Cl and digest with aqua regia) appears to be the most promising giving higher concentration of the elements in all the matrix sample examined.

Key word: metals, compare, methods, soil and sediments

INTRODUCTION

The accuracy of soil quality for agricultural purpose depends solely on the methods used to ascertain the various components of soil elements. The challenges of analytical complexity has been recognized by the soil community and consequence, acceptable precision and accuracy for digestion methods has been reported as typically less than 20% (Voica et al., 2010). The nature of the soil has also provided an avenue of knowledge where soil provides vascular plants with medium for growth, store mineral and trace elements, also its supplies soil organism with most of its nutritional requirements in form of metal elements as component. To ascertain the level of different elemental components of soil the right method must be used. These components can exist in its various forms in soil and different forces keep them bound to soil particles. (Dube et al., 2001)

The distribution of metals in soil and sediments is greatly influenced by activities of organisms, climate, topography, parent's materials and time. (J. Pichtel et al., 1997) but the methods used in determining the level of such elements in the soil is of great concern. Soil represents a matrix with inherent heterogeneity and variable minerals compositions leading to analytical complexity. The determination of metals in soil is challenging and requires the development of various

specific methods. For this reason, three different methods have been compared in this study, the efficiency of digestion or dissociation of the metal elements in solution which depends on the procedures have been evaluated. It is essential to examine thoroughly some of these analytical methods since soil is of utmost importance to plants, human health, livestock and aquatic industries. (Terrance, 2011).

MATERIALS AND METHOD

Sample and Sampling Methods

Samples were taken from Girei Local Government in three specific areas: Batare (BT), Bakalchi and AnguwanHonna (AN). A matrix was formed by mixing 5g of each soil from the three different locations to form a composite of soil samples or matrix. Sampling method carried out is similar to that described by Taylor (2006). Sampling involves the selection from the total population of subset of individuals upon which measurement will be made. (Taylor, 2006) it is also seen as the method of obtaining fraction of bulk material which represents the whole material under analysis.

Sample preparation

Three different (3) digestion methods of sample preparation process were carried-out on each separate portion of the sample matrix.

Method I; Roast before digestion using aqua regia; The required sample (1.0g) of soil sample was transferred completely into crucible and was placed on heating mantle and fire at 105 to 110°C (the temperature was controlled using thermometer) for one hour and was allowed to cooled for two hours in a desicator. The method employed was similar to that of Ehi (2012). The exactly 1g of the soil sample was transferred into kjeldahl digestive flask, 24ml aqua regia solution at the ratio of 3:1 HCl to HNO₃ acid was added to the sample. The 24 ml aqua regia was added and swirled to wet the sample and it was left over night. Next day the flask was placed on hot plate and heated at 60°C to 70°C for 15 minute. The temperature was raise until it boiled for two minutes. The material was then cooled, distilled water was added and make up to 40cm³, the solution was filtered, the filter paper were then washed with 0.25M HNO₃ acid then the 0.25ml HNO₃ was added to mark.

Method II; Air Dried and Digest Using Aqua-regia; the method carried out was similar to the work of Saxena (1990). Soil sample was stored in seal polyethylene container before the arrival at the laboratory. Each of the soil sample collected was spread on a glass slid and air dried for

72hrs before grinding with mortar and pestle, then sieved using 0.2mm nylon sieve. The required sample (1.0g) of soil sample was transferred on glass slide and air dried until a constant weight was obtained and the whole sample was transferred quantitatively into kjeldahl digestive flask and digested with 5cm³ aqua regia and the sample was allowed to stand all night. The next day the sample was swirled and made up to mark with distilled water to 40cm³ and then filtered

Method III; Roast using ammonium chloride before digestion with aqua regia;(Voica C., et al 2010). The required sample (1.0g) of soil sample was weighed and was transferred into crucible. 5cm³ of ammonium chloride was added and mixed and the sample was placed on heating mantle and fired at 105°C to 110°C for 1 hour and allowed to cooled for two hours in a desiccator. Then the sample exactly was transferred quantitatively into kjeldahl digestive flask and 24cm³ Aqua-regia was added. The sample was swirled to wet all the sample and was allowed to stand overnight. The next day distilled water was added and make it up to 40cm³ and then filtered. All the filtrate was quantitatively transfer into sample bottle at the end of each filtration and the absorption of calcium and iron using AAS in each sample respectively and the concentration was traced from the calibration curve obtained.

ANALYTICAL TECHNIQUES

The analytical techniques of the analysis of soil samples involve the use of atomic absorption spectrophotometer (AAS). For determination of essential metals calcium (Ca²⁺) and heavy metals iron (Fe³⁺). Analysis by AAS is based on absorption of electromagnetic radiation by atoms. The absorption of the radiation is proportion to the number of atoms or concentration of the element of interest in the sample. This follows Beer-Lambert Law.

$$A = \log I_0/I_t = abc$$

Where;

A = absorbance of radiation by atom

I = intensities of incidence and transmitted radiation respectively

a = absorptivity constant

b = path length

c = concentration of atomic specie of interest in the sample

Absorbance readings for various standards concentrations was obtained using the same instrument. Various standards were prepared and there absorption was used to plot calibration

curve for each metal elements. The absorbance of the sample element of interest was obtained and the concentration was traced on the standard calibration curve.

The results obtained from the calibration curve have concentration in ppm which was converted to mg/Kg of soil sample using the formular,

$$[\text{metal}] = \text{mg/Kg} = \text{ppm} \times (\text{v/Wt})$$

Where;

ppm = concentration in part per million

v = volume of digested soil

Wt = weight of sample

Sample Mean and Standard deviation was calculated.

RESULT AND DISCUSSION

Results

TABLE 1: Results for Calcium

SAMPLE SITE	METHODS	CONCENTRATION (mgKg ⁻¹)
Matrix Sample	I	416±0.57
	II	444.57±0.94
	III	581.84±1.98

TABLE 2: Results for Iron

SAMPLE SITE	METHOD	CONCENTRATION (MgKg ⁻¹)
Matrix Sample	I	924.48±0.65
	II	852.48±1.68
	III	937.20±1.50

METHOD I; Roastbefore digestion using aqua regia

METHOD II; Air Dried and Digest Using Aqua-regia

METHOD III; Roast using ammonium chloride before digestion with aqua regia

Discussion

All the methods used detect the presence of the metals (Iron and Calcium) in the sample of sample matrix of soil and sediments obtained from three different locations.

From the result obtained as shown in Table 1 which shows the different concentration of Calcium metal in mgKg^{-1} in the matrix sample; Method III shows the highest concentration of the calcium metal. This revealed that the Method extracts the particular metal i.e. Calcium with highest effectiveness and efficiency than the others.

Table 2 shows the different concentration of Iron metal in mgKg^{-1} at different location sites; Method III shows the highest concentration of the Iron metal in the sample matrix.

In general, method III shows the highest concentration of the metals both Calcium and Iron in the different sample matrix of soil samples from different sites locations.

CONCLUSION

The results obtained revealed that for Calcium and Iron metal digestion, method III has the highest sensitivity which gives the highest concentration compare to other methods in the same sample matrix of soil and sediments, in method III the sample of soil have been roasted with an ammonium chloride salt (NH_4Cl). The heating process decomposes the ores of these mineral elements to their oxides, on heating the ammonium salt evaporate leaving mineral acid (HCl), the mineral acid dissolves the oxides of the elements and then treatment with aqua regia extracts the metals elements. (Posypaiko et al., 1984). As shown in Table 1; Methods II has the concentration of the Calcium metals higher than method I but lower than method III. This is probably, because the metals have been converted to their oxides by heating but they have not been digested with any minerals before extraction with aqua regia. The aqua regia function to extracts the metal elements in this case but not as effective and efficient as in the presence of mineral acids. Method I has the lowest concentration. The mineral elements have been extracted from its mineral ore with no pre-treated that decomposes the mineral to its oxides.

Recommendation

This study recommends that further study should be carried out to examine other elements with the same methods that have not been included in this study and other methods should be studied as well.

REFERENCE

- Alloway, B.J (1995). Heavy Metals in Soil. Blackie academic and professional Glasgow. Pg 80-85
- Bollen, Walter B., (1959). Microorganisms and Soil Fertility, Oregon State College, Oregon State Monographs, Studies in Bacteriology, Number 1. pg 22
- Christoph Moor, Theopisti Lymberopoulou & Voker J. Dietrich (2001). Determination of Heavy metals in soils, sediments and geological materials by ICP-AES and ICP MS pg 123-124
- Donahue, Roy Luther, Miller, Raymond W, Shickluna, John C. (1977). Soils: An introduction to soil and plant growth. Prentice-Hall ISBN, 0-13-821918-4
- Dudal R., Nachtergaele F.O & Purnell M.F (2002). The human factor of soil formation, symposium No. 18 paper No. 93 Pg 1-3
- Dube A, Zybztewski R., Kowalkowski T., Cukrowski E., Buszewski B. (2001). Absorption and migration of heavy metals in soil, *publish journal of environmental studies vol.10 No.1, 2001*.
- Ehi-Eromosele C.O., Adaramodu A.A., Anake W.U., Ajanaku C.O., Edobor-Osoh A. (2012) Comparison of Three Methods of Digestion for Trace Metal Analysis in Surface Dust Collected from an E-waste Recycling Site. *Nature and Science* 2012;10(10) <http://www.sciencepub.net/nature>
- ESA21; environmental science activities for the 21st century. Soil composition page 1-6
- Jenny H. (1941). Factors of soil formation, McGraw-Hill, New York NY page 6
- Pichtel J; Sawyerr Ht; Czarnowska K., (1997) "spatial and temporal distribution of metals in soils in Warsaw, Poland", *environmental pollution*, 98(2), pp. 169-174
- Kabala-Pandias A. and H Pandias (1992). Trace elements in soil and plants 2nd edition page 1105-1216
- Lee K.E., (1994). The functional significance of biodiversity in soils, *Trans. 15 World Cong. Soil Sci. Acapulco*, 4a: 168

175 Method 6200. (2007). Field portable x-ray fluorescence spectrophotometer for the determination
 176 of elemental concentration in soil and sediments, February 2007 pg 6200-1
 177 Posypaiko V. I. and Vasina N. A. (1984). Analytical chemistry in metallurgy. First published in
 178 1984, Revised from the 1979 Russian edition. Pg 52– 69.
 179 Scarf R, SCDNR Land, water and conservation division. 25/2/2013@10:06pm pg 1-17.
 180 [Saxena, M. M](#) (1990) English, Book, Illustrated edition: Environmental analysis : water, soil and
 181 air. Agro Botanical Pub., 1990. Environmental chemistry – Technique, Environmental
 182 monitoring India.
 183 Simonson, R. W. (1959). Outline of generalized theory of soil formation. Soil science society of
 184 America proceeding vol. 23 pg 152-156
 185 Soil Survey Staff (1975). Soil taxonomy: a basic system of soil classification for making and
 186 interpreting soil surveys, US department of Agriculture, soil conservation science. US
 187 government printing Office, Washington DC page 1
 188 Sparks L. D. (1995). Ion exchange process environmental soil chemistry. Academic press
 189 London. Pg 11-55
 190 Taylor and Francis group. LLC (2006). Soil sampling and methods of analysis 2nd edition
 191 Terrance Hettipathirana, determination of metals in soils using the 4100 MP- AES pg 1-6
 192 Thornton S. F., Tellam J. H., & Lerner D. N. (2002). Attention of landfill leachate by U.K
 193 Triassic sandstone Aquifer materials. Fate of organic pollutants in laboratory columns.
 194 Journal of contaminants hydrology vol. 43 pg 327-354
 195 Togun A. O., Fawole, Yahye M. K. (2005). Macmillan mastering series for Agricultural Science,
 196 7th edition.
 197 USGS. Contaminant sorption by soil and bed sediment by Science for changing world
 198 Voica C., Dehelean A., Jordache A., Geana I. (2010). Methods validation for determination of
 199 metals in soil and sediments by ICP-MS pg 1-11
 200 Witkamp M. & Frank M. L. (1969). Evolution of CO₂ from litter, humus and subsoil of a pine
 201 stand. Pedobiologia, vol. 9 pg 358-365.