

Original Research Article

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

ABSTRACT

Analytical studies was carried in other to compare the accuracy of three (3) most frequently used methods, in the determination of metals in soil and sediments. Sample of soil and sediments was 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 Benas (2005), Method II: Air dried and digest using Aqua-regia similar to the work of Saxena M.M (1990), and Method III; Roast using ammonium chloride before digestion with aqua regia; (Voica C., et al 2010). The metal elements Calcium and Iron where chosen because of their relative abundance in natural soil and sediments. Results obtained shows that the soil and sediments samples contain the metal element calcium and Iron which were used to examined the accuracy of the three frequently methods that have been used in metals determination in soil and sediments. 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 recognize 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 supply soil organism with most of its nutritional requirements in form of metal element as component. To ascertain the level of different elemental components of soil the right method must be used. These components can exist in 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 influence 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 location to form a composite of soil sample 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

Equipment and Reagents

The equipment that was used for the analysis include; beakers (100ml, 125ml), hot plate or oven, conical flask (250ml), funnels, filter paper (Whatman No.54), reagents bottles, fume cupboard, spatula, analytical balance (AB204 meter Toledo), safety glass, hand gloves and atomic absorption spectrophotometer (AAS). The chemicals that was used for the analysis include; Haloid acid (HCl), Nitric acid (HNO₃), Ammonium chloride (NH₄Cl), Aqua regia (mixture of HNO₃ and HCl in 1:3), Calcium chloride (CaCl₂), Ammonium ferrous sulphate [(NH₄)₂SO₄FeSO₄.6H₂O]

Sample preparation

Three different (3) method of sample treatment process was 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 control using thermometer) for one hour and was allowed to cooled for two hours in a desicator. The method employed was similar to that of Benas (2005). 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 M.M (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 mortal and pistil, then sieve using 0.2mm nylon sieve. The required sample (1.0g) of soil sample was transfered on glass slid and air dried until a constant weight is obtained and the whole sample was transfered 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 make it 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 desicator. 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 involves 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.

$$A = \text{Log } I_0/I_t = abc$$

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 result obtained on 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

This chapter covers all the result of the study as well as the discussion and interpretation of the results obtained.

128 **TABLE 4.1 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

129 **TABLE 4.2 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

130 **METHOD I;** Roastbefore digestion using aqua regia

131 **METHOD II;** Air Dried and Digest Using Aqua-regia

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

133

134 **4.2 DISCUSSION**

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

137 From the result obtained as shown in Table 4.1 which shows the different concentration
138 of Calcium metal in mgKg⁻¹ in the matrix sample; Method III shows the highest concentration of
139 the calcium metal. This revealed that the Method extracts the particular metal i.e. Calcium with
140 highest effectiveness and efficiency than the others.

141 Table 4.2 shows the different concentration of Iron metal in mgKg⁻¹ at different location
142 sites; Method III shows the highest concentration of the Iron metal in the sample matrix.

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

145

Conclusion

The results obtained revealed that for Calcium and Iron metal digestion, method III have 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 4.1; Methods II has the concentration of the Calcium metals higher than method I but lower than method III. This is 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 ammonium salt. 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 study as well.

REFERENCE

- Allow 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, Shicklua, John C. (1977). Soils: And introduction to soil and plant growth. Prentice-Hall ISBN, 0-13-821918-4

175 Dudal R., Nachtergaele F.O &Purnell M.F (2002). The human factor of soil formation,
176 symposium No. 18 paper No. 93 Pg 1-3

177 Dube A, Zybntniewski R., kowalkowski T., Cukrowski E., Buszewski B.(2001). Absorption ad
178 migration of heavy metals in soil, *publish journal of environmental studies vol.10 No.1*,
179 2001.

180 ESA21; environmental science activities for the 21st century. Soil composition page 1-6

181 Jenny H. (1941). Factors of soil formation , McGraw-Hill, New York NY page.6

182 Kabala-Pandias A. and H Pendias (1992). Trace elements in soil and plants 2nd edition page
183 1105-1216

184 Lee K.E., (1994). The functional significance of biodiversity in soils, Trans. 15 World Cong.
185 Soil Sci. Acapulco, 4a: 168

186 Method 6200. (2007). Field portable x-ray fluorescence spectrophotometer for the determination
187 of elemental concentration in soil and sediments, February 2007 pg 6200-1

188 PosypaikoV.I andVasina N.A (1984). Analytical chemistry in metallurgy. First published in
189 1984, Revised from the 1979 Russian edition. Pg 52– 69.

190 Scarf R, SCDNR Land, water and conservation division. 25/2/2013@10:06pm pg 1-17

191 Simonson, R.W (1959). Outline of generalized theory of soil formation. Soil science society of
192 America proceeding vol. 23 pg 152-156

193 Soil Survey Staff (1975). Soil taxonomy: a basic system of soil classification for making and
194 interpreting soil surveys, US department of Agriculture, soil conservation science. US
195 government printing Office, Washington DC page 1

196 Sparks L.D (1995).Ion exchange process environmental soil chemistry.Academic press
197 London.Pg 11-55

198 Taylor and Francis group. LLC (2006). Soil sampling and methods of analysis 2nd edition

199 Terrance Hettipathirana, determination of metals in soils using the 4100 MP- AES pg 1-6

200 Thornton S.F, Tellam J.H, &Lener D.N (2002).Attention of landfill leachate by U.K
201 Triassicsandstore Aquifer materials. Fate of organic pollutants in laboratory columns.
202 Journal of contaminants hydrology vol.43 pg 327-354

203 Togun A.O, Fawole, Yahye M.K (2005). Macmillan mastering series for Agricultural Science,
204 7th edition.

205 USGS. Contaminant sorption by soil and bed sediment by Science for changing world

- 206 Voica C., Dehelean A, Jordache A., Geana I. (2010). Methods validation for determination of
207 metals in soil and sediments by ICP-MS pg 1-11
- 208 Witkamp M. & Frank M.L. (1969). Evolution of CO₂ from litter, humus and subsoil of a pine
209 stand. *Pedobiologia*, vol. 9 pg 358-365.