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EFFECT OF PRETREATMENT ON THE DETERMINATION OF METAL CONTENT IN A NATURAL BARITE MINERAL

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ABSTRACT

Two pretreatment methods (Liquid- Liquid Extraction Method, LLEM and Wet Digestion Method,WDM) of samples prior to Atomic Absorption Spectroscopy analysis for metal content were investigated for optimum yield using Atomic Absorption Spectrometry (AAS) on three barite samples. The range of concentration of the fifteen metals by LLEM was 0.25±0.11 – 3,760± 9.59mg/kg and that of WDM was 0.85±0.15 - 3,585± 11.85mg/kg. Some metals were detected by LLEM which were not detected by WDM probably due to evaporative losses. Although, WDM led to the quantitative determination of more metals than LLEM but LLEM led to the determination of the highest concentration of barium, the chief metal in barite which is used in drilling mud. However, there was no statistically significant difference in the metal concentration of the samples in the two methods of pretreatment. Therefore, for solid minerals like barite, a complementary use of the two methods is advised.

Key Words: Weight digestion method, Liquid- liquid extraction method, Nasarawa State, Barite, Atomic absorption spectroscopy, metals

INTRODUCTION

Increasing levels of metals in the environment from various anthropogenic sources has become a source of concern for environmentalists. Unlike the toxic organics that in many cases can be degraded, the metals that are released into the environment tend to persist indefinitely, accumulating in living tissues through food chain (Gossich et al; 2000)

Increasing awareness about ecotoxicological effects of metals has resulted in more stringent legal requirements for reduction in industrial emission. However, the relative impact of elevated metal concentration is expected to be controlled by the dominant form of the metals present (Oviasogie et al; 2008).

In almost all geographic areas, drilling grade barites are environmentally acceptable from the standpoint of disposal as part of the used drilling fluid (Bruton et al., 2006). Barite used in oilfield application is regulated for chemical purity as it is recognized that some sources of barite may contain heavy metals ranging from trace amounts to some exceeding 3% by weight. The industry has recognized that discharges of heavy metals may cause environmental damage and potentially human health problems. Due to the allowable and significant discharge of barite-laden drilling fluids, most countries' regulatory bodies set maximum allowable levels of heavy metals in barite such as a mercury(Hg), calcium (Ca), Zinc (Zn), Strontium (Sr), Iron (Fe), Tin (Sn), cadmium (Cd) and lead (Pb) content. The maximum API specification for some heavy metal such as Pb, Cd, Hg and Ca or Mg are 1000mg/kg, 5mg/kg, 5mg/kg, 250mg/kg respectively (Ken and Clifford, 2001, Bruton et al; 2006). Besides, these metals or minerals associated with barite also cause problems in certain mud systems, and tend to reduce the expected API specification of barite(4.2) for drilling mud (Baroid,1996).

Therefore, a carefully selected pretreatment method (digestion) preceding a chosen instrumental method of analysis is necessary for the optimum determination and assessment of the mineral matrix metals for accurate decision making.

Depending on the technique used for final elemental measurement, sample preparation can vary from none to quite extensive ones. The most widely employed technique in elemental analysis of petroleum and petroleum related materials are the atomic spectroscopy with flame, non -flame or plasma atomizers (Nadkarni, 1991). Application of this technique using various sample preparation methods have been widely reported (Akpan, 2005, Udo et al., 1992 and Asuquo et al., 1994).

In this investigation, the wet digestion and liquid- liquid extraction methods were comparatively explored.

MATERIALS AND METHODS

The barite used in this investigation is the discordant vein type obtained from Azara, Obi Local Government Area of Nasarawa State, Nigeria (Figs. 1a & b)

A

Figure: 1a

B

Figure: 1b

Discordant, vein type in Azara area

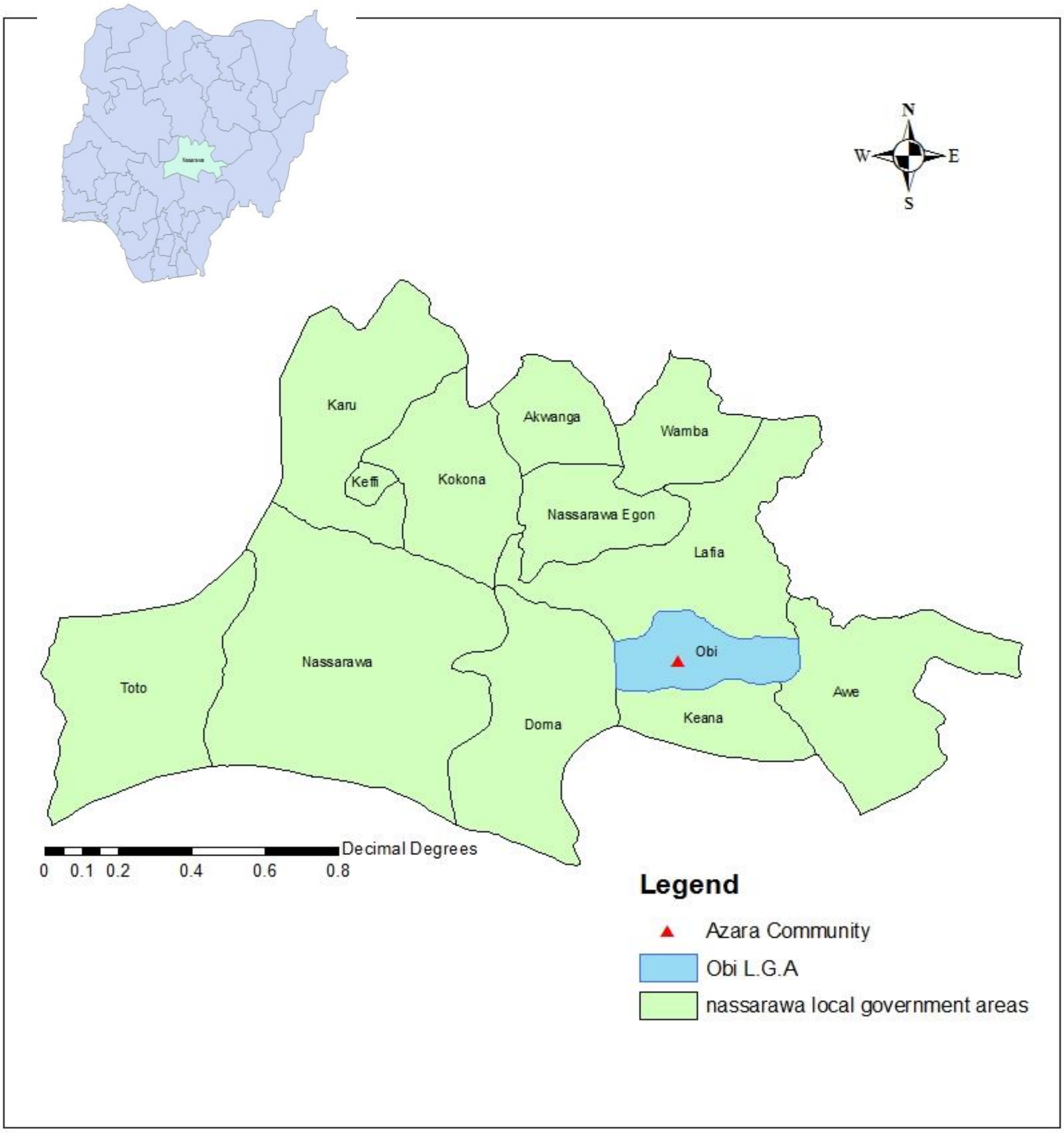

Figure 2: Map of the Nasarawa State, Nigeria Showing Sample Location.

Location of the Study Area

The study area is located in Azara, Obi local government area, Nasarawa State, Nigeria (Figure 1). It is situated within the Lower Benue Trough within latitudes N08° 21′□10″, longitude E09° 04′□36″□and latitude N09° 36′□12″, longitudes E09° 24′□24″, respectively (Offodile, 1976).

The coordinates of the various locations were also duly taken (latitude N08° 22’ 0”, longitude E09° 15’ 0”; latitude N08° 32’ 0”, longitude E09° 18’ 0” and latitude N08^{o} 44’ 0’’, longitude E 09^{o} 21’ 0’’for samples A_1, A_2 and A_3 respectively).

Sampling

Three different local samples were collected from veins of barite in Azara, Nasarawa State as indicated in the location of the study area, by using a geologic hammer to chip out the barite sample and duly labelled.

Sample Preparation

The barite samples were crushed using mortar and pestle. The crushed samples were then sieved to pass through vibrating screen of 0.600mm mesh size.

Sample digestion

***Liquid-liquid extraction method (LLEM)*:** 0.5g of the sieved sample was dissolved in 20ml of Chloroform ($CHCl_3$); the resulting solution was poured into a separating funnel containing 20ml of 10% Nitric acid (HNO_3). After thorough shaking and phase separation, the $CHCl_3$ layer (denser phase) was separated from HNO_3 layer (less dense phase) containing metals. The HNO_3 layer was drained into a 50ml volumetric flask and made to mark with distilled water (Akpan, 2005)

Blank was prepared similarly except that no sample was used.

***Wet digestion method* (WDM):** 0.5g of the sieved sample was digested in a kjeldahl flask using 4ml of concentrated tetraoxosulphate(VI) acid (H_2SO_4). The mixture was heated to 70^{o}C in a fume cupboard until it charred (ashing process). The charred sample was re-digested using 4ml of 50% hydrogen peroxide (H_2O_2). Another 4ml of caro acid, H_2SO_5, (a mixture of 85% H_2SO_4 and 50%H_2O_2) was added and the sample was heated until it turned colourless. After cooling, the sample was transferred into a 50ml volumetric flask and made up to mark with distilled water (Akpan, 2005).

A blank was prepared similarly except that no sample was used.

Determination of the Metal Content

The digested samples were thereafter analysed for their metallic contents using atomic absorption spectrophotometer (AAS), Model: A-Analys 100 equipped with relevant elemental hollow cathode lamps and digital display read out. Triplicate readings were taken for each metal and their mean concentrations (mg/kg) and standard deviation calculated. Analysis of variance (ANOVA) for the metal concentrations of the three samples qobtained from the two methods was done at 0.05 confidence level.

RESULTS

The results of the metal concentrations obtained from the different methods are presented on table 1; and the descriptive statistics shown as figures 3- 5

Table 1: Concentrations of metals by methods

Metals	Sample A_1		Sample A_2		Sample A_3	
	Metal concentration by method (mg/kg)					
	LLEM	WDM	LLEM	WDM	LLEM	WDM
Calcium	709±3.10	1343±7.98	236± 5.15	3.60± 2.50	200± 10.50	40±7.50
Magnessium	64.4±2.55	114± 6.27	28.0±3.62	99.6± 2.75	80±11.35	150±10.50
Iron	62.2±4.21	351± 5.65	162±7.35	3585± 11.85	250±15.15	600± 12.75
Zinc	1.60±0.05	1.67± 0.65	7.60±9.25	616± 4.95	59.55± 6.35	355± 12.35
Copper	160±1.15	31.0± 3.86	98.6± 9.21	2.16± 1.55	201±11.25	25.15±9.25
Lead	6.00±1.56	20.2± 1.35	130±8.65	17.6± 3.75	30.50±5.0	100.75±0.25
Cadmium	1.60±2.60	175± 6.70	1.60±7.89	197± 4.95	70.50±8.55	185± 8.25
Vanadium	1.60±1.20	4.56± 1.25	3.60±0.75	3.36± 1.45	4.40± 3.55	8.10±2.55
Barium	1760±7.65	384± 10.35	3760±9.59	744± 5.85	1500±11.65	475± 4.50
Tin	21.0±1.60	36.7± 3.75	13.0±2.50	31.9± 5.95	39.40±5.35	49.35±10
Chromium	1.10±0.21	ND	ND	ND	2.45±2.50	11.25±5.35
Manganese	0.88±0.34	2.89±0.45	1.95±2.85	ND	3.75±3.50	15.45±4.50
Nickel	2. 24±0.25	4.32± 1.45	2.20± 0.35	3.75±0.55	3.75±4.40	9.55±3.30
Cobalt	0.25±0.11	0.85±0.15	ND	ND	7.70±2.55	15.35±4.30
Iron	5.65±1.25	8.65±1. 85	0.95±0.35	1.21±0.35	4.55±0.55	15.65± 5.35

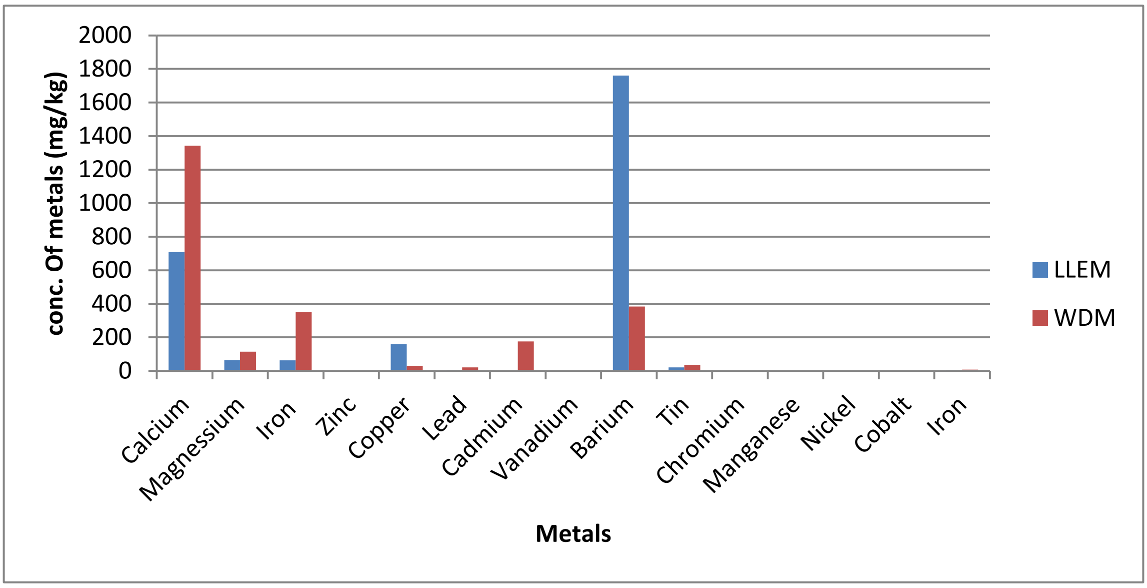

Figure 3: Comparative Chart of LLEM and WDM for Sample A1

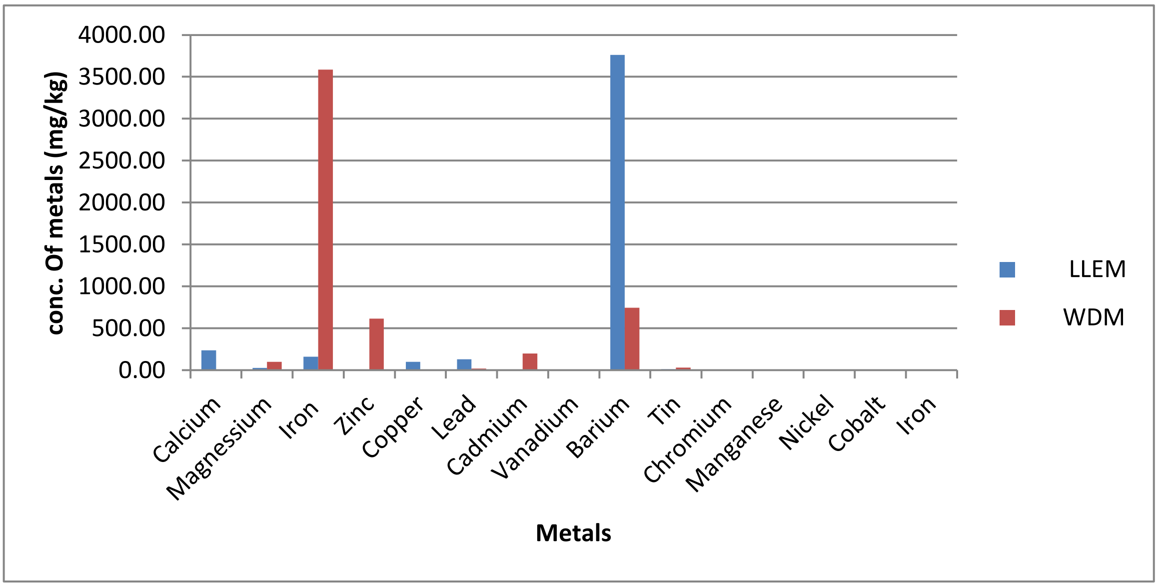

Figure 4: Comparative Chart of LLEM and WDM for Sample A2

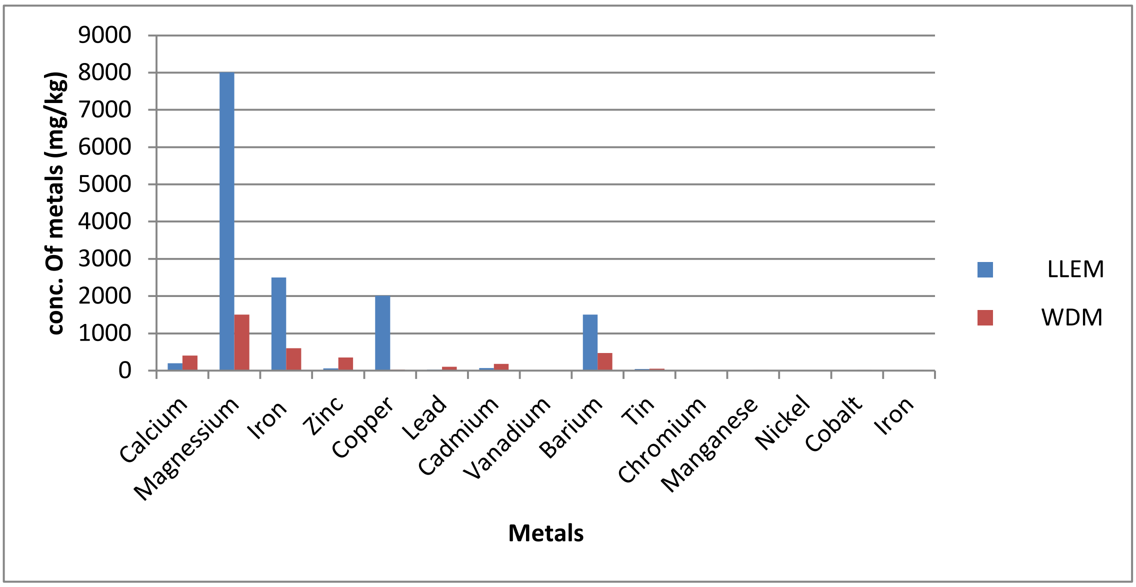

Figure 5: Comparative Chart of LLEM and WDM for Sample A3

DISCUSSION

Barium had the highest mean concentrations in the three samples by liquid- liquid extraction method (LLEM) - sample A_1 (1,760±7.65mg/kg); sample A_2(3,760±9.59mg/kg) and sample A_3(1,500±11.65mg/kg) while cobalt had the least concentration in the three samples by liquid- liquid extraction method- sample A_1(0.25±0.11mg/kg); though it was not detected at all in sample A_2 and chromium as well was not detected. Therefore, the range of metal concentrations obtained by LLEM was 0.25±0.11 – 3,760± 9.59mg/kg

The results of the weight digestion method (WDM) showed that iron had the highest concentration, sample A_2 (3,585± 11.85mg/kg) while cobalt had the least concentration, sample A_1(0.85±0.15 mg/kg). However, cobalt and chromium were not detected at all in sample A_2 by both methods. Therefore, the range of metal concentrations obtained by WDM was 0.85±0.15 - 3,585± 11.85mg/kg.

In samples two and three, more metals were quantitatively measured by the Atomic Absorption Spectrometer following the wet digestion (WDM) pretreatment method than the liquid- liquid pretreatment method. In sample two equal numbers of metals were quantitatively measured.

However, the analysis of variance (ANOVA) for the metal concentrations of the three samples at 0.05 confidence level gives the significance level between the methods as 0.879 which is above the confidence limit of 0.05. Therefore, there is no significant difference between the concentrations of the metals obtained from the two methods in the three samples.

This is not in good agreement with the results obtained from crude oil samples from the Niger Delta, Nigeria and crude oil samples from the North Alaskan using the same pretreatment methods by Udo et al; 1992, Akpan, 2005; and Curiale, 1987 where the WDM pretreatment led to a significantly higher yield of metal concentration than the LLEM pretreatment.

One would have expected the WDM, where strong oxidizing agents such as tetraoxosulphate(vi) acid (H_2SO_4) and hydrogen peroxide (H_2O_2) were used, to lead to a significantly higher metal concentrations than the LLEM. This is because the reagents have the ability to destroy organic matrices and release associated metals compared to LLEM where strongly associated metals may not be extracted by the technique. However, the fact that barium, which is the chief metal in barite mineral, was quantitatively extracted more by LLEM than WDM indicates that the organic matrix of barite mineral may not be strongly associated with the barium metal, even though barite is a solid mineral.

Few elements like chromium and cobalt that were not detected by WDM but were detected by LLEM may be due to evaporative losses during the digestion of the samples by WDM (Akpan, 2005).

Since there was no statistically significant difference between the two pretreatment methods, they may be used complementarily in the evaluation of metal contents of solid minerals like barite for use in drilling mud.

There was no statistically significant difference between the metal concentrations of the three barite samples pretreated by the wet digestion method and by the liquid – liquid extraction method. This is however contrary to the results obtained from crude oil samples from the Niger Delta, Nigeria and crude oil samples from the North Alaskan using the same pretreatment methods where the WDM pretreatment led to a significantly higher yield of metal concentration than the LLEM pretreatment. The fact that they are different organic matrices may have been responsible for the observed difference. Therefore, the two methods may be used complementarily in the evaluation of metal contents of solid minerals like barite for use in drilling mud.

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REFERENCE

Akpan, I. O. (2005). Effect of sample treatment on trace metal determination of Nigerian crude oils by Atomic Absorption Spectroscopy Technique. African Journal Environmental Pollution and Health, 4(1): 1-5

Asuquo, F.E., Morah, F., Nya, A.E. and Erhardi, M. (1994). Trace element in crude oils and beach tar from Nigerian coastline. Indian Journal Marine Science., 24: 16- 18.

Baroid, J.V. (1996). Invests in Barites, World of Minerals: Industrial Minerals, No. 347, P.14.

Bruton, J.R.S., Bacho, J. S., Newcaster J.A. and Swaco, M.I. (2006). Society of Petroleum

Engineers. pp. 1-7.

Cossich, E.S., Tavres ,C.R.G. and Ravagnani, T.M.K (2000). Biosorption of chromium(111) by

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© Faculty of Science, University of Port Harcourt, Printed in Nigeria ***ISSN 1118 – 1931***

Sargassum sp Biomass, Electronic Journal of Biotechnology 5(2): 30-37

Curiale, J.A. (1987). Distribution of transition metals in North Alaskan oils. J. American Chemical Society, 344: 135 – 145.

Ken, A.P. and Clifford, J.H. (2001). Circular No. 4, Mineral Resource Engineer. pp 2-3

Nadkarni, R. A.(1999). A review of modern instrumental methods of elemental analysis of petroleum related materials. ASTM STP, 1109: 19-51.

Offodile, M.E. (1976). A Review of the Geology of the Cretaceous Age of the Benue Valley. In Geology of Nigeria (C.A. Kogbe Ed.) Univ. Ife, pp. 319-330.

Oviasogie, P.O., Aghimien, A.E. and Ndiokwere, C.L.(2008). Fractionation of Ni and V in wetland soils and their distribution in tissues of the oil palm. J. Chem. Soc. Nigeria. 33(2): 113-123.

Udo, O.T., Ekwere, S. and Abrakassa, S. (1992). Some trace metals in selected Niger Delta crude oils: Applications in oil- oil correlation studies. J. Min. Geol., 28(2): 289- 292.