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Determination of Vanadium, Nickel, Copper and Iron as Complexes of Bis-Acetylpivalyl Methane (Ethylene Diamine) in Nigerian onshore and offshore Crude Oils Using HPLC

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Abstract

Higher performance liquid chromatographic determination of vanadium, nickel, copper and iron was conducted from Nigerian Crude oil samples obtained from Nigerian Petroleum Development Company (NPDC). The procedure was based on complexation of the analytes with bis (acetyl pivalyl methane) ethylenediamine (H_2APM_2en) followed by solvent extraction and HPLC separation on a reverse phase, C18, 5µm column. The complexes were eluted with methanol : acetonitrile : water (60:20:20) at a flow rate of $1cm^3$/min. and uv detection at 260nm.The results show that nickel had the highest concentration while copper had the least concentration. The concentration levels of these elements in the crude oil samples range from 210 – 1620 ppb for Ni, 975 – 1125ppb for Fe, 225 – 1060ppb for V, and 54 – 138ppb for Cu. The pattern of occurrence for each element agreed with earlier studies using Niger Delta oils. The results indicate that trace metal data compliment well with the organic geochemical data and trace metals are useful in oil classification. It was obvious from this study that Nigerian crude have low metal content. However, despite the low concentrations, they could still pose an intrinsic health hazard considering their cumulative effect in the environment.

Keywords: key words, Crude oil, Heavy metals, HPLC

1. Introduction

Crude oil is a naturally occurring, flammable liquid found in rock formations in the Earth consisting of a complex mixture of hydrocarbons of various molecular weights, and other organic compounds. The hydrocarbons in crude oil are mostly alkanes, cyclo alkanes and various aromatic hydrocarbons while other organic compounds contain nitrogen, oxygen and sulfur, and trace amounts of metals such as iron, nickel, copper and vanadium. The exact molecular composition varies widely from formation to formation but the proportions of chemical element vary over fairly narrow limit as follows: Carbon (83-87%), Hydrogen (10-14%), and Nitrogen (0.1-2%), Sulphur (0.5-6%), Oxygen (0.1-1.5%), Metals (<1000ppm) (Speight, 1999).

The determination of metals content in crude oil is an important part of any crude oil quality program. Even though the oil is typically desalted prior to distillation, small amounts (<1ppm) of some elements (i.e. Pb, As, Ni, V, Hg, and Cu) remaining in the oil can rapidly deactivate some refinery catalysts or end up product. Therefore, the determination of the metals concentration in crude oil before and after processes such as desalting is of value to refinery operation (Nadkarni, 1991).

Crude petroleum oils contain vanadium, nickel, iron and copper as organically bound metals mostly as metalloporphyrins and metallo non-porphyrins (Gondal *et al.*, 2006). Their determination is of considerable importance, because the metal complexes may poison and foul catalysts or cause undesirable side reactions in refinery operations, such as fluid cracking and hydrodesulphurization. A number of analytical methods have been used for the determination of metal ions in crude petroleum oils, including Atomic Absorption Spectrometry (AAS), (Duyck *et al.*,2007), inductively-coupled plasma atomic emission spectroscopy (ICP-AES) (Al-swaiden,1996), radioisotope x-ray Fluorescence (Alvarez *et al.*, 1990), neutron activation (Adeyemo *et al.*, 2006), and liquid chromatography (khuhawar *et al.*,1998).

This study is aimed at using high performance liquid chromatography, in the determination of metals in crude oil. This will give a simple and quickest way of assessing the Nigerian crude oils, impact in the environment and economic potentiality. The objectives of the research are:-

(i) To identify the heavy metals (Fe, Ni, V, and Cu) in the crude oil samples obtained
(ii) To quantify the identified elements
(iii) To compare the parameters in terms of heavy metals concentration.

The work will be limited to the determination of vanadium, nickel, iron, and copper in Nigerian crude oils due to their abundant and adverse effects in refinery operations.

2.0 Materials and Methods

2.1 Materials

The apparatus used in this research work are the normal routine laboratory apparatus which include Weighing balance, Hot plate, PH meter, Microsorb C-$_{18}$ column, Rheodyne 7125 injector, Hitachi D2500 chromatographic integrator. Prominence HPLC apparatus.

2.2 Reagents

All the reagents were of purity and HPLC grade, they include Concentrated nitric acid, Concentrated sulphuric acid, Perchloric acid, Methanol, Sodium Acetic acid, Acetonitrile, Bis(acetylpivalylmethane) ethylenediimine. Sodium hydride, Ethyl acetate,Chlororoform, ethylenediamine, Diethyl ether.

2.3 Methods

2.3.1 Samples Collection

Nigerian crude oil samples from onshore and offshore wells were collected from Nigerian Petroleum Development Company (NPDC) Benin City. The crude oil samples were obtained from five different oil wells namely: Okkoro (onshore), Oredo (onshore), Oziengbe (onshore), Okkono (offshore) and Okpoho (offshore).The samples were labeled as A for Okkoro, B for Oredo, C for Oziengbe, D for Okkono, and E for okpoho.

2.3.2 Preparation of Reagents

1M Sodium Acetate-Acetic Acid Buffer (pH 6)

Sodium acetate (9.82g) was dissolved in 90cm^3 of distilled water. The pH of the solution was adjusted to 6.0 with 2M acetic acid and the volume was made up to 100cm^3 with distilled water (Sambrook *et al.,* 2006).

1 %W/V (H_2APM_2en) Solution in Methanol

Bis (acetylpivalylmethane) ethylenediimine (1 gram) was dissolved in 100cm^3 of methanol (Lanjwani *et al*., 1996).

Standard Solution

An aliquot of solution (1- 5cm^3) containing 0.5 - 2.0ppm of vanadium, nickel, iron and 0.05 - 0.02ppm copper was prepared. Further dilution was performed to prepare the standard solution for calibration curves. These are equivalent to 500 – 2000ppb for vanadium, nickel, iron and 50 – 200ppb for copper respectively. (Lanjwani *et al*., 1996).

2.3.3 Analysis of Standard Solution

The standard solutions 5cm^3 containing vanadium, nickel, iron and copper was transferred to a well-stoppered test tube and sulphur dioxide was passed for 1min. 2cm^3 of 1M Sodium acetate-acetic acid buffer pH 6 was added and the contents were heated gently to near dryness.5cm^3 of bis (acetylpivalyl methane) solution (1% w/v in methanol) was added and the contents were heated for 15-20 min. During heating the volume of the solution was reduced to about 1 cm^3. 2cm^3 each of Water and chloroform were added and the contents were shaken well. The layers were allowed to separate and exactly 1 cm^3 of the chloroform layer was transferred to a sample vial. The solvent was evaporated and the residue dissolved in 1cm^3 methanol. 5µl of the methanolic solution was injected onto a Microsorb C- 18, 5 µm column (150 x 4.6 mm id.) and complexes were eluted with methanol: acetonitrile: water in the ratio of (60:20:20) at a flow rate of 1cm^3 min^{-1} . Detection was achieved using a UV monitor fixed at 260 nm (Lanjwani *et al*., 1996).

2.3.4 Analysis of the Crude Oil Samples

10g of the crude oil samples were transferred to a beaker and 40cm^3 sulphuric acid (98%) was added. The contents were heated on a hotplate until white fumes of sulfur trioxide was evolved. The mixture was allowed to partially cool, 40cm^3 of nitric acid (65%) was added slowly and the contents were heated gently. 20cm^3 Perchloric acid (72%) was added drop wise to maintain vigorous oxidation with excessive evolution of brown fumes of nitrogen oxides. The clear solution was heated to near dryness. The residue was dissolved in water and the volume was adjusted to 25cm^3. 12 cm^3 aliquot of the solution was taken; the pH was adjusted to 6 using 2cm^3 1M sodium acetate- acetic acid buffer. The contents were heated gently to near dryness. 5cm^3 of bis (acetyl pivalyl -methane) solution (1% w/v in methanol) was added and the contents were heated for 15-20 min. During Water heating the volume of the solution was reduced to about 1 cm^3. 2cm^3 each of Water and chloroform were added and the contents were shaken well. The layers were allowed to separate and exactly 1 cm^3 of the chloroform layer was transferred to a sample vial. The solvent was evaporated and the residue dissolved in 1cm^3 methanol. 5µl of the methanolic solution was injected onto a Microsorb C- 18, 5 µm column (150 x 4.6 mm id.) and complexes were eluted with methanol: acetonitrile: water in the ratio of (60:20:20) at a flow rate of 1 cm^3 min^{-1} . Detection was achieved using a UV monitor fixed at 260 nm (Lanjwani *et al*., 1996).

2.3.5 Linear Calibration Curves

Linear calibrations graphs were prepared by by plotting the average peak area against concentration of each metal ions in (ng) as shown in fig. 1-4 below, and fig. 5 represent the typical chromatogram of the sample and standard used for the analysis. The peak areas were obtained from the chromatogram as shown in fig.5. finally the concentration of the metal ions in the samples were evaluated from the calibration curves.

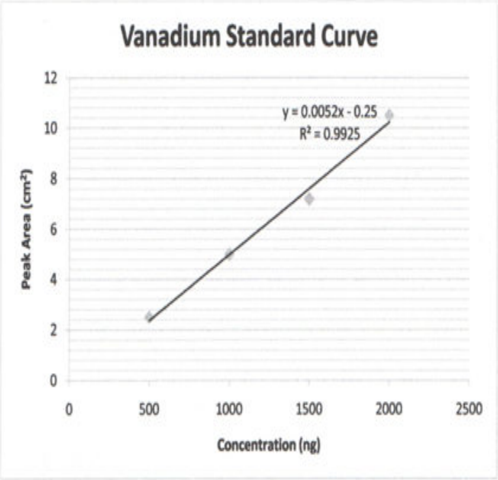

Fig.1

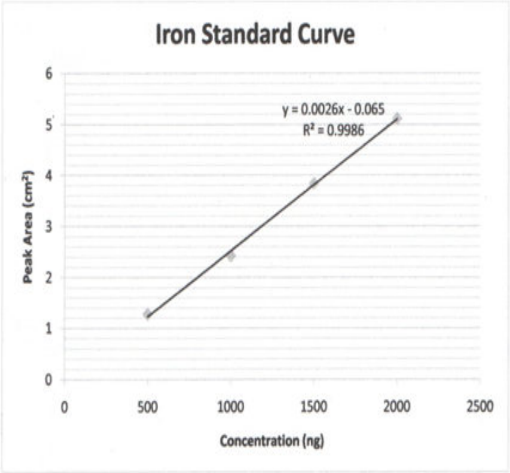

Fig.2

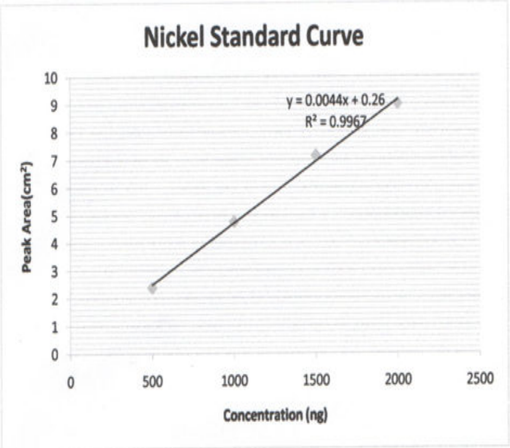

Fig.3

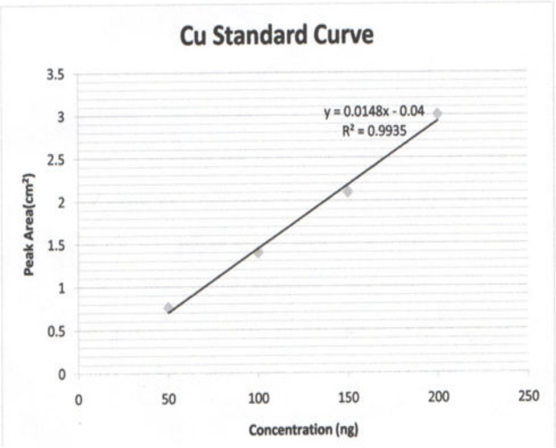

Fig.4

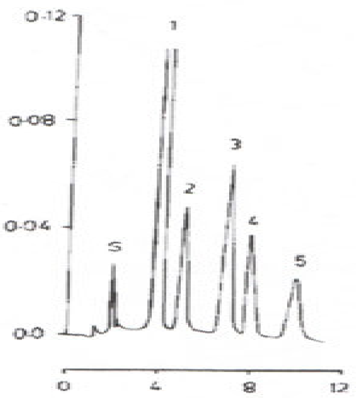

Fig.5: HPLC chromatogram of a typical sample used for this analysis containing S= solvent, 1= reagent, 2 = oxo-vanadium (iv) (1060ng/ml), 3= iron (ii) (1130ng/ml), 4= nickel (ii) (1442ng/ml), 5= copper (ii) (64ng/ml) with peak areas of 5.03, 2.86, 6.33, and 0.91 cm^2 respectively. Eluent: methanol, acetonitrile and water. Flow rate: 1ml/mint. Detection: UV at 260nm.

3. Results and Discussion

3.1 Results

Table 1: Concentration of heavy metals in the crude oil samples analyzed.

CRUDE OIL SAMPLES	Metal Concentration (ppb) Fe	Cu	Ni	V
A	975±2.8	133±0.8	1400±4.1	300±0.8
B	1125±4.1	63±0.81	1550±6.5	1060±5.7
C	1025±8.9	54±3.3	1620±5.7	655±7.1
D	1050±5.7	60±1.6	1450±9.8	490±6.5
E	1055±4.1	138±1.6	210±8.9	225±8.9
AVERAGE	1046±5.1	89.6±1.6	1246±7.0	546±5.8

Key: Results were presented as mean ± standard deviation of triplicate analysis. A = Okkoro, B = Oredo, C = Oziengbe, D = Okkono, and E = Okpoho.

Table 2: Comparisons Of Trace Metals Data Obtained From The Present Study And Trace Metals Data Obtained From other studies.

STUDY	**Cu**	**Fe**	**Ni**	**V**
Present study ranges (ppb).	54 – 138	975 – 1125	210 – 1620	225 -1060
Akinlua *et al.,* 2007 (ppb).	3.31 – 19.4	11.4 – 1241	26.3 -144.1	11.2 –29.2
Nwanchukwu *et al.,* 1995(ppb).	540 -42307	6 – 25073	351 -11282	9– 1832
Olu OluWole *et al.,* (1993) (ppb).	1860 – 18900	3400 – 9540	540 – 5030	540 – 1195
Udo*etal.*,1992 (ppb).	30 – 70	60 – 360	4400-6900	3700-40000
Ndiokwere,1983 (ppb).	ND	ND	2200-5600	100– 642
Olajire and Oderinde 1995(ppb).	50 – 54000	43000 -11000	5000-11000	14000 – 99000

Key: ND ---------- Not detected

3.2 Discussion

The results of metal concentrations (ppb) obtained from this study are indicated in Table 1 .The mean values of the concentrations determined were of the order Ni > Fe >V > Cu. This trend is consistent in all the crude samples analyzed except for the last sample (E) where Ni reported second to the least value instead of the highest value. Ni had the highest concentration among the metals studied in all the samples while copper had the least concentration. The distribution of the metals is fairly homogenous in the samples. These may be connected to the difference in geological activity, source rock type, depositional environment and maturation (Akinlua *et al.*, 2007).

Iron

From Table 1 iron concentrations range from 975 – 1125 ppb with an average of 1046 ± 5.1ppb. Comparing these result with studies from Niger Delta oils, Akinlua *et al.*, (2007) (Table 2) reported 11.4 – 1241 ppb with an average of 177.36 ppb. There is good agreement between the two results but the average of latter is higher. Considering other studies as indicated in Table 2, the results obtained from this study is higher than the values of 60 - 360 ppb reported by Udo *et al.,* (1992) and lowers than the values of 3400 – 9540 ppb and 43000 – 110000 ppb reported by Oluwale *et al.,* (1993) and Olajire and Oderinde (1995) respectively (Table 2). But the results are within the range of 6 – 25073 ppb reported by Nwanchukwu *et al.,*(1995) (Table 2).The presence of iron (Fe) in the petroleum samples analyzed may alter the selectivity and activity of the catalyst in the cracking of petroleum (Monaco *et al.,* 1993; Ismagilov, 2003), if not removed before refining.

Copper

From Table 1 copper ranges from 54 – 138 ppb with an average of 89.6 ± 1.6 ppb. These values are lower than the values of 540 – 42307 ppb and 1860 – 18900 ppb obtained by Nwachukwu *et al*., (1995) and Oluwale *et al*., (1993) (Table 2) but higher than the values of 3.31 – 19.4 ppb obtained by Akinlua *et al*., (2007) and within the range of 30 - 70 ppb and 50 – 54000 ppb reported by Udo et *al*., (1992) and Olajire and Oderinde (1995) respectively (Table 2). The presence of copper in the petroleum markedly alters the selectivity and activity in cracking reactions if allowed to accumulate on the catalyst before refining (Monaco *et al.,* 1993; Ismagilov, 2003).

Nickel

Nickel concentrations from Table 1 range from 210 – 1620 ppb averaging 1246± 7.0 ppb. These values are higher than the values of 26.3 – 144.1 ppb obtained by Akinlua *et al*., (2007) (Table 2) but lower than the values of 4400 – 6900 ppb, 2200 – 5600 ppb and 5000 – 11000 ppb obtained by Udo et *al*., (1992), Ndiokwere (1983) and Olajire and Oderinde(1995)(Table 2). Also the results are within the range of 351 – 11282 ppb and 540 – 5030 ppb reported by Nwachukwu *et al*., (1995) and Oluwale *et al*., (1993) (Table 2). The presence of nickel in the petroleum also alter the selectivity and activity of the catalyst in the cracking of petroleum if allowed to accumulate on the catalyst thereby affecting product performance (Monaco *et al.,* 1993; Ismagilov, 2003), if not removed before refining.

Vanadium

The values of vanadium range from 225 – 1060 ppb with an average of 546 ± 5.8 ppb (Table 1). The values are higher than the values of 11.2 – 29.2 ppb reported by Akinlua *et al*., (2007) (Table 2) but the average is within the range of 100 – 642 ppb reported by Ndiokwere (1983) (Table 2). Also the results are lower than the values of 3700 – 40000 ppb and 14000 – 99000 ppb obtained by Udo et *al*., (1992), Olajire and Oderinde (1995) (Table 2). The results also agreed with the range of 9 – 1832 ppb and 540 – 1195 ppb reported by Nwachukwu *et al*., (1995) and Oluwale *et al*., (1993) (Table 2). The presence of vanadium in the petroleum analyzed can cause toxic pollutants. Relatively higher vanadium content can affect refinery equipment, distillation units, lining of industrial furnaces and loss of thermal efficiency (Nakayama *et al*., 1997). Therefore vanadium content should be reduced to the barest minimum level before refining.

TABLE 2

Table 2 shows the range of concentrations covered by this study and the range reported by other studies. The crude samples used by these studies were obtained from different region of Niger Delta area and therefore can be use to evaluate the present study. It is evident from the studies presented in Table 2 that transition metals have been found to be very useful in crude oil characterization especially in oil –oil correlation studies. Oils from marine organic matter have higher concentration of metals (particularly Ni and V), this is expected since for marine source rocks there is abundant input of porphyrin-precursor chlorophylls to the organic matter derived from algae and bacteria. Moderate quantities of metals are found in oils derived from lacustrine source rocks while little nickel and vanadium is found in land plant derived oils. Nickel has been found to correlate positively with the absolute amount of heavy n-alkanes in petroleum and is relatively more abundant in paraffinic petroleum. Enriched vanadium and nickel concentrations greater than 100ppm are observed in bitumens that are associated with type II kerogens. Bitumens associated with type III kerogens contained vanadium and nickel concentrations less than 100ppm. It is also reported from these studies that source rock type and depositional environment have a profound effect on the predicted levels of nickel and vanadium in the source rocks, and there is systematic variation in the nickel and vanadium content of crude oils which can be related to depositional environment and source rocks types. This implies that the source rock type depositional environment determines the proportion of vanadium and nickel in crude oils. API gravity is also inversely correlated with each of copper, nickel and vanadium. Higher concentration of metals are only associated with crude oils of low to moderate API gravity. Total transition metal content decreases with increase oil maturity and the highest concentration of metals are in low maturity crude oils. From the above correlation of parameters (i.e origin of the crude oil, type of the crude oil, maturity and API gravity of the crude oil), the following order can be assigned for the crude samples analyzed.

(i) Marine / terrestrial origin: B > C > D > A > E.

Sample B have the highest marine/terrestrial input with E having the least.

(ii) Heavy n-alkanes / paraffin's: C > B > D > A > E.

Sample C have the more heavy n-alkanes /pararaffins with sample E having the least.

(iii) API gravity / maturity: E > A > D > C > B.

Sample B has the highest API gravity and is the most matured with sample E having the least API gravity and is less matured.

5. Conclusion

Determination of Fe, Ni, Cu, and V was conducted using higher performance liquid chromatography. The results obtained showed that the Nigerian crude oil oils have low metals contents. From the data generated from this research work, the crude oils analyzed were derived from organic matter deposited in more oxidizing transitional environments. The abundance of paraffin as indicated by higher concentration nickel revealed that these oils were derived from organic matter of mixed terrestrial ⁄ marine input with a preponderance of terrestrial organic matter. Also from the distribution patterns of the metals analyzed the oils are matured and genetically related. Finally, the patterns of occurrence of the elements determined are in good agreement with the studies conducted using Niger Delta oils. The technique used in this analysis provides a new route for simultaneous determination of other trace elements in crude oil.

6. Recommendation

In view of the results obtained from this study, the following recommendations are hereby forwarded.

(a) There is need for chemists to explore the cheapest mean of synthesizing bis(acetylpivalylmethane) ethylene diimine and other complexing reagents that can be used in HPLC in other to make this method of analysis as cheap as AAS or even more cheaper.

(b) Since the concentration of metals in Nigerian crude oils is very low, HPLC would be one of the best methods for the detection of these metals, because the detection limits is up to ng/g (ppb).

(c) Considering the cumulative effects of these metals in the environment, an efficient control means for the release and discharge of petroleum and petroleum products should be established to protect the workers, community and the environment from the hazards of these metals.

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