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SARA Separation and Determination of Concentration Levels of Some Heavy Metals in Organic Fractions of Nigerian Crude Oil

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Abstract:

Nigerian Crude oil samples were obtained from Nigerian Petroleum Development Company (NPDC). The samples were subjected to column chromatography. Sequential leaching method was used to separate the crude oil into four distinct fractions based on leaching of crude oil with different organic solvents and mixtures. Saturated fraction was extracted with hexane- cyclohexane (1:1v/v), aromatic fraction was extracted with hexane- toluene (7:3v/v), while resin was extracted with tetrachloromethane-trichloromethane (7:3v/v), and asphaltene was extracted with acetonitrile-methanol (1:1v/v). The fractions were digested using sulphuric acid, nitric acid and hydrochloric acid method followed by the detection of metals in the samples using AAS analysis. The elements analyzed were Pb, Cu, Cr, Fe and Ni. The result shows that Fe had the highest concentration while Ni had the least concentration. The concentration (ppm) levels of these elements in the crude oil fraction analyzed range from 0.1307 – 0.4107 for Pb, 0.1796 – 1.1250 for Cu, 2.7420 – 10.1903 for Cr, 11.2962 – 21.8084 for Fe, and 0.0464 – 0.5876 for Ni. It was obvious from this study and previous ones that Nigerian crude oil fractions have low metal content. However, despite their low concentrations they can still be detrimental to the refinery operations and the immediate environment, and therefore, should be removed before refining.

Keywords: Atomic Absorption Spectroscopy, Aromatic, Asphaltenes, Risens, Saturates, Heavy Metals

1. Introduction

Petroleum consists predominantly of hydrocarbons, and contains measurable quantities of many metals. Nickel and vanadium are commonly the most abundant metals. Other metals such like Fe, Ni, Zn, Ca, Cu, Cr, Pb, Mn, and Co are present in low concentrations. The nature of these metals and their abundance in crude oils can give information on the origin, migration and maturation of petroleum as well as providing a basis for regional geochemical prospecting. The nature of metals in crude and residual oils is of interest to the refinery operator and to the environmentalists concerned with the emissions from the oil fired power plants. Vanadium, nickel, iron and copper are normally found in petroleum as naturally occurring elements associated to the formation process and although present only in small amounts (μg g−1 or ng g−1 levels), they are very important to the petroleum industry . Their determination is of considerable importance, since they have deleterious effects on refinery operation and performance. They may corrode refinery equipment, poison and foul catalysts and/or cause undesirable side reactions in refinery operations (Brandao *et al.,* 2007).

1.1 Chemical Composition of Crude Oil

Even though crude oil consists of tens of thousands of different hydrocarbon molecules, the properties of the elements in crude oil vary over fairly narrow limits. A wide variation in properties is found from the lightest crude oils to the highly asphaltenic crudes. The carbon content normally, is in the range of 83-87%, and the hydrogen content varieties between 10 and 14%. In addition, varying small amounts of nitrogen, oxygen, sulfur and metals are found in crude oils (James, 1999).

Due to the complex composition of crude oil, characterization by the individual molecular types is not possible and elemental analysis is unattractive because it gives only limited information about the constitution of petroleum due to the constancy of elemental composition. Instead, hydrocarbon group type analysis is commonly employed with the knowledge of the distribution of major structural classes of hydrocarbons. Crude oil is needed in various fields in the petroleum industry. Example, are studies related to reservoir evaluation, migration and maturity degradation process, processing and environmental effects (Ronningsen *et al.,* 1990). The SARA-separation is an example of such group type analysis, separating the crude oils into four main chemical classes based on differences in solubility and polarity. The four SARA-fractions are saturates, aromatics, resins and asphaltenes. The method is based on the sequential leaching of crude oil with different organic solvents and mixtures. Saturate hydrocarbons on percolation in an n – pentane eluant are not absorbed on activated silica. The saturate fraction of the oil is eluted from the column with n – pentane at 5mL/minute. The solvent is removed using a rotary vacuum evaporator to recover the saturate fraction. Aromatic hydrocarbons are adsorbed on activated silica in the presence of n – pentane and desorbed by toluene at 5mL/minute. The resin fraction of the oil is eluted from the chromatographic column using toluene – methanol solution. Asphaltene fraction is eluted with acetonitrile – methanol solution (Mansoori, 1997).

This type of analysis is very simple to perform and has found wide application in the petroleum industry (Barman *et al.,* 2000). As the physical and chemical characteristic of crude oils and refined products differs significantly, several methods have been developed and standardized to study their SARA composition. Several SARA analysis methods based on open column, low – pressure liquid chromatographic separation using polar stationary phases such as alumina, silica and fluorosil are reported (Elsa *et al.,* 1994). Saturates are usually eluted with n – alkane solvents, this is followed by the elution of aromatics, resins and asphaltenes with solvents of increasing polarity. The solvent strength can be enhanced by mixing more than one solvent to get improved separation between compounds classes. Silica gel is the preferred stationary phase for the separation due to its good stability, although alumina can better separate the aromatic fractions based on the number of aromatic rings. (Elsa *et al.,* 1994).

1.2 Saturates

The saturate (aliphatic) are non-polar hydrocarbons, without double bonds, but including straight-chain and branch alkenes as well as cycloalkanes (naphtenes). Cycloalkanes contain one or more rings, which may have severely alkyl side chain. The proportion of saturates in a crude oil normally decrease with increase molecular weight fraction. Thus, saturates generally are the lightest fraction of the crude oil. Wax is a sub-class of the saturate, consisting primarily of straight-chain alkenes, mainly ranging from C_{10} to C_{30}. Distribution of n – alkanes has been used to differentiate the petrogenic and biogenic contribution in complex environmental samples. Usually the n–alkanes with an odd number of carbon atoms are found in higher concentrations if the crude oil is derived from a biogenic source. On the other hand, the concentration of n – alkanes decreases with an increase in the carbon number if it is derived from a petrogenic source. The distribution of n-alkanes in crude oils can be used to indicate the organic matter source (Duan, 2000). Generally, short and medium chain odd carbon numbered compounds of aliphatic hydrocarbons with carbon numbers between n-C_{15} and n-C_{25} are associated with aquatic sources, where shorter derivatives originates from lacustrine algae in contrast to mainly macrophyphic plants as sources of the longer chain derivatives(Ficken *et al.,* 2002). Hector *et al.,* (1990) reported n-alkanes range from C_{10}-C_{35} with slight odd-over-even predominance, maxima at n-C_{15}-C_{20} and ratios n-C_{12}-C_{31}/n-C_{15}-C_{20} indicating a moderate wax content. Akinlua *et al.,* 2007 identified saturated hydrocarbons ranging from n– alkanes (C_8 – C_{40}), hopanes and steranes in northwestern Niger Delta oils, Nigeria.

1.3 Aromatic

The term aromatic refers to benzene and the structural derivates. Aromatic are common to all petroleum and by far the majority of the aromatic contain alkyl chains and cycloalkane rings, along with additional aromatic rings. Aromatic are often classified as mono, di-, and tri-aromatics depending on the number of aromatic rings present in the molecule. Polar, higher molecular weight aromatics may fall in the resin or asphaltene fraction. Crude oil contains a wide variety of aromatic hydrocarbons ranging from mono aromatics hydrocarbons such as benzene to poly aromatic hydrocarbons (PAHs) with many fused aromatic rings. More than 85% of the aromatic hydrocarbons in crude oil contain one or more alkyl substituent on their aromatic rings. Aromatic compounds containing sulphur and nitrogen atoms in the ring e.g. (thiopenes) are also very common in crude oil (Wang *et al.,* 1994).

Aromatic hydrocarbons are important constituents of petroleum and extract of both recent and ancient sediments (Radke *et al.,* 2001). PAHs are not synthesized in living organisms and almost absent in natural organic matter. The majority of PAHs in petroleum are the products of complex chemical transformations of naphthenic and/or olefinic biological ancestors during diagenesis and catagenesis. Abundance of certain aromatic hydrocarbons in crude oils and sediments such as 1,2,5 – trimethyl naphthalene, 1,2,5,6 – tetramethylnaphthalene, 9- methylphenanthrene, 1,7 – dimethyl phenanthrene originate from diterpeniod and triterpenoid natural products. The most useful application of aromatic hydrocarbons is evolution of thermal maturity of organic matter (Radke *et, al.,* 2001).

1.4 Resins

This fraction comprised of polar molecules often containing heteroatoms such as nitrogen, oxygen or sulphur. The resin fraction is operationally defined as the fraction soluble in light alkanes such as pentane and heptane, but insoluble in liquid propane. Since the resins are defined as a solubility class, overlap both to the aromatic and the asphaltene fraction is expected. Despite the fact that, the resin fraction is very important with regard to crude oil properties, little work has been reported on the characteristics of the resins, compared to for instance the asphaltenes. However, some general characteristics may be identified. Resins have a high H/C ratio than asphaltenes, 1.2 - 1.7 compared to 0.9 - 1.2 for the asphaltenes. Resins are structurally similar to asphaltenes, but smaller in molecular weight (>1000g/mol). Naphthenic acids are commonly regarded as part of the resin fraction (Ficken *et al.,* 2002).

1.5 Asphaltenes

The asphaltenes fraction, like the resins, is defined as a solubility class, namely, the fraction of the crude oil precipitating in light alkanes like pentane, the hexane or heptanes. This precipitate is soluble in aromatic solvents like the toluene and benzene. The asphaltenes fraction contains the largest percentage of heteroatoms (O, S, N) and organometallic constituents (Ni, V, Fe) in the crude oil. Asphaltene are believed to be suspended as a micro colloid in the crude oil, consisting of particles of about 3mm each. The particles consist of one or more atomic sheets of asphaltene monomers with absorbed resin acting as surfactants to stabilize the colloid at suspension (Ficken *et al.,* 2002).

1.6 Metals in Crude Oils

Crude oils primary constituents are organic but also contain trace concentrations of inorganic or metals in the range of subparts per billion (ppb) to tens and occasionally hundreds of parts per million (ppm). The trace content of metals in crude oil is of interest for the potential contamination of the environment. Environmental risks depend on the toxicity and concentration of each metal in the crude oil. High concentrations of metals in soil and water can be harmful to land, marine animals, and plants, upsetting delicate ecological balances and contaminating food sources (Carey *et al.,* 2004). Crude oil is particularly rich in certain metals, such as vanadium, which reaches 2000ppm in Venezuelan crude oil. Most alkalis and alkaline earth metals are present in small amounts of order of ppm or less (Manning and Gize, 1993).

1.7 Sources of Trace Metals in Crude Oil

Metals in petroleum arise from several source, produced oil will contain metal distribution from original source rock, organic matter, from metal leached during migration and after emplacement in reservoir (Curiale, 1987).

1.8 Mode of Occurrence of Metals in Crude Oil

Trace metals are incorporated into oils inform of porphyrin complexes (Species) in petroleum source rocks and may include direct incorporation from the biomass and formation during sedimentation, it may also involve digenesis from organic molecules as well as metal derived from different biogenic (biomass) and abiogenic (weathering of minerals) source (Manning and Gieze, 1993).

1.9 Significant of Metals in Crude Oil

Metals are present in crude oil at concentration levels from few parts-per million in heavy crudes to parts-per billion in light crudes. The negative effects of metals include the catalyst poisoning and fouling, corrosion of equipment and particulate emissions into the environment, and the contamination of petroleum-related products. On the other hand, the metals are often used as tracers in geochemical prospecting. Their isotopic ratios are used for oil-oil or oil-source rock correlation or for identification of the source rock depositional environment and in the quantification of the oils thermal maturity and biodegradation levels (Caumette *et al.,* 2009). Ratios such as vanadium to vanadium plus nickel and iron to vanadium are suggested as being useful for oil type characterizations. Transition elements concentrations and ratios can serve as excellent oil-oil correlation parameters. Generally, vanadium and nickel content increases with asphaltic content of crude oil (API gravity is an indicator). The lighter oils contain less metal (Caumette *et al.,* 2009).

In diesel fuels, vanadium can form low melting compounds (e.g. V_2O_5, melts at 691^0C) and cause several corrosive attack on all the high temperature alloys used in the gas turbine blades and diesel engine valves, vanadium in fuel should be < 2ppm; at 10ppm vanadium, the corrosive rate is as thrice as high, and at 30ppm vanadium, it is thirteen times much. However, if sufficient magnesium is present in the fuel, it will combine with vanadium to form higher melting compounds and reduce the corrosion. Sodium and potassium combine with vanadium to form low melting eutectics (565^{0}C). Hence, sodium and potassium in the gas turbine fuels must be limited (Boldt and Hall, 1977). If not removed in the fuel treatment process, a high level of sodium will give rise to post combustion deposits in the turbocharger. These can normally be removed by water washing (Reynolds, 2001). Calcium is not harmful from a corrosion stand points, actually it helps to inhibit the corrosive action of vanadium. However, calcium can form hard bonded deposits which are not readily removed. Lead can cause corrosion and spoil the beneficial inhibiting effect of magnesium additives on the vanadium corrosion (Boldt and Hall, 1977). Combine with sodium and vanadium complexes, sulfur forms deposits on the external surfaces of super heater tubes, causing equipment corrosion and loss of thermal efficiency (Boldt and Hall, 1977).The harmful effect of heavy metals, on human health, environment and refinery equipments call for the assessment of the concentration of heavy metals in organic fractions of Nigeria crude oils. This will give an indication to the fractions of Nigeria crude oils. This will give an indication to the fraction that is heavily burden with these metals, and therefore, appropriate measures can be taken in handling such fractions, in order to avoid problems associated with the heavy metals such as catalyst poisoning, clogging of refinery linings and equipments as well as other problems that are directly concern to human health and environment.

This study is aimed at investigating and comparing the concentration levels of Pb, Cu, Cr, Fe and Ni in organic fractions of Nigerian crude oils. This will help in assessing the Nigeria's crude oil impact on the environment and its economic potentiality.

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, Filter paper, Desiccator, Beaker, Volumetric flask, Digestion flask, Hot plate, $_P$H meter and AAS machine.

2.2 Reagents

All the reagents were of analytical standard and include Acetonitrile, Acetone, Chloromethane, Paraffin liquid, Cyclohexane, Butanol, Methyl alcohol anhydrous, concentrated hydrochloric, concentrated sulphuric acid, concentrated nitric acid, n- Hexane, Methanol, Tetra chloromethane, Toluene, Silica gel, Xylene, and Ethanol.

2.3 Methods

Preparation of reagents

The solvents used were prepared as described below:

a) Hexane: cyclohexane (1:1): 125cm^3 of hexane was measured into a 250cm^3 volumetric flask and made up to mark with cyclohexane (Caumette *et al.,* 2009).
b) Hexane: toluene (7:3) 70cm^3 of hexane was measured into a 100cm^3 volumetric flask and made up to mark with toluene (Caumette *et al.,* 2009).
c) Tetrachloromethane: chloromethane (7:3): 70cm^3 of tetrachloromethane was measured into a 100cm^3 volumetric flask and made up to mark with chloromethane (Caumette *et al.,* 2009).
d) Acetonitrile: methanol (1:1):125cm^3 of acetonitrile was measured into a 250cm^3 volumetric flask and made up to mark with methanol (Caumette *et al.,* 2009).
e) 3% Nitric acid (HNO_3): 3cm^3 of concentrated HNO_3 was pipette into a 100cm^3 volumetric flask and made up to mark with distilled water (Caumette *et al.,* 2009).

2.3.1 Sample Collection and Treatment

The crude oil sample was collected from Nigeria petroleum development company (NPDC) Benin City in well cleaned sample bottles. Sequential leaching method was used to separate the crude oil into distinct fractions. The method is based on leaching of crude oil with different organic solvents and their mixtures. Sequential leaching allows the separation of four hydrocarbons fractions:

- Saturated hydrocarbons (extracted with 1:1 (v/v) hexane – cyclohexane mixture).
- Aromatic (extracted with 7:3 (v/v) hexane – toluene mixture,
- Resins (extracted with 7:3 (v/v) $CCl_4 – CH_3Cl$ mixture), and
- Asphaltenes (extracted with 1:1 acetonitrile methanol mixture) (Caumette *et al.,* 2009).

Isolation and characterization of the fractions from the crude Purification of the adsorbent (silica gel), 150g of silica gel (100 – mesh) was washed with 400mL of ethanol in a refluxing apparatus for 2 hours. The silica gel was then dried in the oven and stored in a desiccator (Caumette *et al.,* 2009).

2.3.2 Isolation of fractions from crude oil by column chromatography

The silica gel was introduced into the column and homogenized with hexane. 10g of the crude oil sample was introduced into the glass column and eluted with hexane: cyclohexane (1:1), pale yellow band (saturated fraction) was collected in a sample bottle. It was then eluted with hexane: toluene (7:3), a yellow band (aromatic fraction) was collected. Then, tetrachloromethane: dichloromethane (7:3) was used; a wine red band (resins) was collected. Lastly, acetonitrile: methanol (1:1) was used; a black band (asphaltenes) was extracted into sample bottle. The procedure was applied for the crude oil sample to obtain the fractions (Caumette *et al.,* 2009).

2.3.3 Treatment of the Fractions for AAS Analysis

Sulphuric acid, Nitric acid and Hydrochloric acid Method was used for the digestion. 1g of sample was mixed with 1g of finely grounded potassium permanganate and then 2cm^3 of concentrated H_2SO_4 was added while stirring. A Strong exothermic reaction occurred. The mixture was treated with 2cm^3 of concentrated HNO_3 followed by 10cm^3 of concentrated HCl and heated until there was no evolution of gas. The mixture was filtered and the residue was washed with hot concentrated HCl; the residual was transferred to a digestion flask, heated with 5cm^3 of concentrated HCl and filtered. The filtrate was heated at temperature below 150^{0}C to drive off excess HCl, then transferred to a 100cm^3 volumetric flask and made to the mark with distilled water (EPA, 1996).

2.4 Preparation of blank solution for AAS analysis

The procedural blank used to eliminate possible contaminations was prepared from the sample preparation procedure to contain the same volume of reagents used, except the sample (Walinga *et al.,* 1989).

3. Result and Discussion

3.1 Result

Table 1: Result from Physical Examination of the Sample /Fractions

Sample /fractions	Physical examination/ observation
Crude oil sample	Dark- brown oily fluid
Saturate fraction	Pale- yellow oily liquid
Aromatic fraction	Yellow oily liquid
Resin fraction	Wine red liquid
Asphaltene fraction	Dark brown – black suspended solid

Table 2: Concentration of Heavy Metals in Crude Oil Fractions

Sample	Metal Concentration (ppm)				
	Pb	Cu	Cr	Fe	Ni
A	0.1307±0.041	0.4097 ±0.010	3.8991 ±0.063	14.5472 ±0.052	0.1469 ±0.045
B	0.2907 ±0.062	1.1250 ±0.041	10.1903 ±0.064	21. 8084 ±0.044	0.0464 ±0.034
C	0.2027 ±0.062	0.1796 ±0.024	2.7420 ±0.033	11. 2962 ±0.028	0.2938 ±0.043
D	0.4107 ±0.057	0.6695 ±0.043	6.7727 ±0.017	16.7618 ±0.017	0.5876 ±0.063

Key: Results were presented as mean ± standard deviation of triplicate analysis.

A= Saturate fraction, B= Aromatic fraction, C= Resin fraction, D=Asphaltene fraction

3.2 Discussion

The results from the physical examination of the sample and the fractions are as presented in Table 1. The crude oils sample is dark-brown oily fluids. Saturated hydrocarbon fraction is a pale -yellow oily liquid, aromatic fraction is yellow oily liquid, resin fraction is wind red liquid, and asphaltene fraction is dark brown- black suspended solid. In general, for each crude oil, the colours of the fractions deepen on proceeding from non-aromatics to aromatics. Thus colour can be used to characterize the fractions collected during column chromatography of crude oils and petroleum products. The results agree with those reported by Odebunmi *et al.* (2002). The results of metal concentrations (ppm) obtained from this study are indicated in Table 2 .The mean values of the concentrations determined for sample A were of the order Fe > Cr > Cu > Ni > Pb. For sample B and D, Fe > Cr > Cu > Pb > Ni. For sample C the trend was Fe > Cr > Pb > Cu > Ni. This trend was only consistent in samples A and D, and different trends were observed for sample A and C. Fe had the highest concentration among the metals studied in all the samples while Ni 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). The knowledge of metal content of crude oil sample is important for designing demetallization process and evaluation of its effectiveness (Saitoh *et al.,* 2001). The zinc in the crude oils may poison catalyst in the cracking of petroleum (Pearson and Green, 1993; Ismagilov, 2003), if not removed before refining.

Iron

From Table 2, iron concentrations range from 21.808-11.26ppm. Aromatic fraction had the highest concentration of Fe followed by asphaltene fraction, saturate fraction and resin fraction. The presence of iron (Fe) in the petroleum fractions analyzed may alter the selectivity and activity of the catalyst in the cracking of petroleum (Monaco *et al*., 1997; Ismagilov, 2003), if not removed before refining.

Chromium

The values of chromium from table 2, ranged from 10.1903 – 2.7402ppm. The aromatic fraction had the highest concentration of chromium followed by asphaltene, saturate and resin fractions. The presence of chromium in the petroleum fractions analyzed can cause toxic pollutants. Relatively higher chromium content can affect refinery equipments, distillation units, lining of industrial furnaces and loss of thermal efficiency (Nakayama *et al.,* 1997). Therefore chromium content should be reduced to the barest minimum level before refining.

Copper

From Table 2, copper ranges from 1.1250 – 0.1796 ppm. The aromatic fraction had the highest concentration of copper, followed by asphaltene, saturate and resin fractions. The presence of copper in the petroleum fractions markedly alters the selectivity and activity in cracking reactions if allowed to accumulate on the catalyst before refining (Monaco *et al.,* 1997; Ismagilov, 2003).

Lead

The values of Pb range from 0.4107 – 0.1307 ppm. The asphaltene fraction had highest concentration of lead, followed by aromatic, resin and saturate fractions. The presence of lead in the petroleum fractions analyzed can cause toxic pollutants. Relatively higher lead content can affect refinery equipments, distillation units, lining of industrial furnaces, and loss of thermal efficiency (Nakayama *et al.,* 1997). Therefore lead content should be reduced to the barest minimum level before refining.

Nickel

Nickel concentrations from Table 2 range from 0.1469– 0.0048ppm. The saturate fraction had the highest concentration of nickel followed by resin, aromatic and asphaltene fractions. The presence of nickel in the petroleum fraction 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.,* 1997; Ismagilov, 2003), if not removed before refining.

5. Conclusion

Determination of iron, chromium, copper, lead and nickel in Nigerian crude oil fractions was conducted using Atomic Absorption spectrometry (AAS). From the results obtained asphaltene fraction had the highest concentration of Pb and Ni, while the aromatic fraction had the highest concentration of Cu, Cr and Fe, followed by, saturate and resin fractions. The results obtained showed that the Nigerian crude oil fractions have low metals contents. Finally, the patterns of occurrence of the elements determined are in good agreement with the studies conducted using Niger Delta oils.

6. Recommendations

In view of the result obtained from this study, the following recommendations are hereby suggested.

a. An efficient Governmental controls for industrial and municipal discharge should be established especially for petroleum and petroleum products discharge.
b. More effort should be emphasize for effective removal of metals from crude oil before refining to ensure total eradication of their harmful effects.

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