



## Trace element characterization of crude oil, petroleum products and waste from the Tema Oil Refinery in Ghana using instrumental neutron activation analysis

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### ABSTRACT

A total of 14 different Petroleum samples comprising of 4 crude oil blends, 7 refined products and 3 wastes from the Tema oil refinery were analyzed for 27 elements using Instrumental Neutron Activation Analysis (INAA). Based on the results obtained and analytical procedure used in this work, pattern of occurrence of the metal contaminants in the petroleum products and waste suggest they are native to the crude oil and its origin as no external contamination was established. It was observed from the study and previous ones that the Brass and Bonny crude oil from Nigeria have low metal contents. However, despite the low concentrations, trace amounts of these metals could be deleterious in the refinery as they can cause corrosion, catalytic poisoning, and affect the quality of refined products. They could also contribute to environmental pollution as results of combustion of fuel products and hence should be reduced or removed.

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### Introduction

A very critical and an important component of an environmental management system is the maintenance of an emission inventory. One of the main aims of the inventory is to test the effectiveness of governmental environmental policies and to evaluate to what extent policy targets for emission reduction are achieved. In this regard the quality or validity of the data on which the inventory is based is of paramount importance.

Most heavy metal emissions are the result of industrial activity, and one of the identified potential sources is the oil industry; either directly through stack emissions from refineries or indirectly from emissions resulting from combustion of hydrocarbon fuels[1].

In order to assess the magnitude of metal emission by the oil industry it is necessary to have an accurate knowledge of the metal content of the crudes which the industry processes.

From a literature study carried out in the early 1990s [1] it became clear that data on the metal content of crudes, except for vanadium and nickel, were scarce and often showed a very large scatter.

The Tema oil refinery (TOR) has two main crude processing units; the Crude Distillation Unit (CDU) and the Residual Fluid Catalytic Cracking (RFCC) unit with feed capacities of 45000 and 14000 barrels per stream day of crude oil respectively. The crude distillation unit was designed to process Brass River, Bonny light and Bonny Medium Crude all from Nigeria with densities in the range  $25.2 < \text{API} < 42.8$ . Currently various crude blends (coco/brass/ medanito/ bonny/ baobab etc) in the same density range are being processed.

The physical operations of refining, such as vaporization, fractionation and cooling are governed to a large extent by the properties of the hydrocarbons that constitute the bulk of the crude oil.

Crude oil which is made up various hydrocarbons streams also contains contaminants such as inorganic salts (e.g NaCl, MgCl<sub>2</sub> and CaCl<sub>2</sub>) and organic salts. Associated with these salts are trace metals such as Vanadium (V), Nickel (Ni), Sodium (Na), Calcium (Ca) and Iron (Fe).

Knowledge of the constituents of crude oil to be processed is very important to the refiner in order to know the level of contaminants in crude oil before desalting and after desalting to help plan desalting and chemical injections. Effective desalting will help reduce scaling in equipment, reduction in corrosion especially at the crude column overhead lines and to obtain good quality residue which serves as a feed to the RFCC Unit. High levels of contaminants such as Na, Ca, V, Ni and Fe in the Residual Fuel Oil (RFO) which serves as feed to the Residual Fluidized Catalytic Cracking (RFCC) Unit may poison the catalyst used in the catalytic [2-4].

Conventional methods commonly employed for trace metal analysis in crude oil and petroleum products include atomic absorption spectrometry (AAS), inductively coupled plasma-optical emission (ICP-OES) and mass spectrometry (ICP-MS), X-ray fluorescence (XRF), and instrumental neutron activation analysis (INAA). Among these, instrumental neutron activation analysis (INAA) comes with high precision, accuracy, sensitivity coupled with the ease of sample preparation (Shah et al 1970; Landsberger 1994; Cam et al 1997).

In spite of these merits associated with usage of INAA in studies of trace metals concentration, its application in Ghana as far as petroleum samples are concerned has received little attention [4,5].

In this work, a nuclear analytical technique (Instrumental Neutron Activation Analysis) has been used to measure trace metals in 14 different petroleum samples comprising of 4 crude

oil types, 7 product types and 3 wastes types obtained from crude oil refining process. This will help compliment the conventional techniques used at the refinery and to achieve results in terms of product quality, corrosion control, preservation of RFCC catalyst at the Tema oil refinery and provide accurate data on emission estimate resulting from either directly through stack emissions from refinery or indirectly from emissions of combustion of hydrocarbons

## Materials and Methods

### Description of Study Area

The study area is located in Tema, one of the industrial cities in Ghana. It is found on the equator and the Greenwich Meridian (zero line of longitude) on the West Coast of Africa. The Tema township has a population of 141 479 according to the year 2000 census [6]. About 30 major industries including the country's main harbour are located in this city. The main occupations of the inhabitants are factory work and fishing.

The TOR located at latitude 5°40'10.24"N and longitude 0°00'25.18"E was incorporated on 12 December 1960 as Ghanaian Italian Petroleum Company limited. The refinery covers a total area of 440 000 m<sup>2</sup> and is linked to an oil jetty at Tema harbour by pipes of various diameters for the transportation of crude oil and petroleum products. The refinery has two main crude processing units: the crude distillation unit (CDU) and the residual fluid catalytic cracking (RFCC) unit with capacities of 45 000 and 14 000 barrels per stream day of crude oil, respectively. The refinery sludge mainly from the heat exchangers and residue are accumulated in a waste holding pit. Scales from the refinery equipment removed during periodic maintenance are deposited around the waste holding pit.

### Sampling and Sample Preparation

Sampling was carried out at the two processing units: CDU and the RFCC. Four crude oil types, namely; coco crude oil, brass and bonny crude blend, brass and coco crude blend all from Nigeria and bonsu crude oil from Saltpond in Ghana, were sampled for this work. The petroleum products collected include light naphtha, heavy naphtha, light gasoil, heavy gasoil and kerosene, refined from the brass and bonny crude blend were sampled from the CDU plant. The residual fuel oil and gasoline refined from the residual fuel oil was also sampled from the RFCC plant. Samples from the field were stored in a refrigerator at temperatures between 16 and 22°C in the laboratory and later prepared according to the protocol of the laboratory for irradiation. The waste samples made up of sludge (dry) mainly from heat exchangers accumulated over the years in a waste holding pit within the refinery and scales from refinery equipment and tubing removed during periodic maintenance and deposited around the waste holding pit were also sampled. The residual mud water from the CDU plant obtained after desalting of crude and disposed as sewage was sampled. A total of 60 samples were collected from the refinery. These comprised of samples of crude oil, products and waste. Three samples of each sample type were used and average found.

Prior to irradiation, Samples of Crude oil, petroleum products and residual mud water samples were prepared by weighing 500mg of the sample into a smaller polyethylene capsule (previously soaked in concentrated nitric acid and washed with distilled water to remove any surface contamination). A piece of clean cotton wool (pre-weighed) was put gently into the sample in the vial, capped, and heat sealed. The samples were double encapsulated by putting the smaller polyethylene capsule of diameter 1.2cm and height 2.3cm containing the samples in to bigger polyethylene irradiation

capsules (rabbit capsules) of diameter 1.6cm and height 5.5cm and a piece of clean cotton wool added for packing and then capped and heat-sealed. Two sets of each sample were prepared with each set made of 3 replicates. Single standard elements 10ppm and 20 ppm from the US National Institute of Standard and Technology (NIST) were equally prepared in the same way as the samples for internal quality control. A control vial with only cotton (no sample) was also packaged for background analysis [4,5].

The sludge and scale samples were prepared by weighing 0.1 g of the samples into a clean polyethylene film and sealed using soldering rod, labelled and put into a rabbit capsule capped and heat sealed. Similarly, standard reference materials IAEA Soil -7 and GBW07107 of equal weights were prepared the same way as the scale and sludge samples.

### Sample Irradiation and Counting

The prepared samples and standards were irradiated in the inner pneumatic irradiation sites of the Ghana Research Reactor one centre (GHARR-1) at the Ghana Atomic Energy Commission, operating at half full power of 15 KW with a thermal flux of  $5 \times 10^{11}$  n.cm<sup>-2</sup> s<sup>-1</sup>. Samples were transferred into irradiation sites via pneumatic transfer system at a pressure of 0.6 Mpa. The samples irradiations were categorized into two schemes, one for short-lived radionuclides and another for medium to long-lived radionuclides. For Crude oil, petroleum products and residual mud water samples irradiation times (ti) ranged from 3mins to 1 h and a decay time (td) of 10s for short-lived radionuclides, 24hrs for medium-lived radionuclides and 2-4weeks for long-lived radionuclides. Irradiation times for scale and sludge samples also ranged from 10s to 1h with decay time as stated above. The irradiation scheme used for analysis of a particular sample was done by optimizing irradiation time (ti), decay time (td) and counting time (tc) based on the half life (t<sub>1/2</sub>) of the respective elements.

Induced radioactivities in samples after the irradiation were measured by a PC-based  $\gamma$ -ray spectrometry set-up. It consisted of an n-type high purity germanium (HPGe) detector Model GR 2518 (Canberra Industries Inc.) coupled to a computer based PCA-MR 8192 multi-channel analyser (MCA) mounted in a cylindrical lead shield (100 mm thick) and cooled in liquid nitrogen with a resolution of 1.8 KeV (FWHM) for <sup>60</sup>Co gamma-ray energies of 1332 KeV and a peak-to-Compton ratio of 55:1. The detector operated on a bias voltage of -3000V with relative efficiency of 25% to NaI detector. Through appropriate choice of cooling-time, detector's dead time was controlled to be less than 10%. Identification of the  $\gamma$ -ray of product radionuclides was through the energies and quantitative analysis of the concentration was obtained using the  $\gamma$ -ray spectrum analysis software, ORTEC MEASTRO-32. The quantitative analysis was done by converting the counts as area under the photopeak of the radionuclides by the comparator method[7] (Landsberger 1994) using the same geometry, equal weights of both sample and standard, with the same irradiation, decay and counting times. The analytical photopeaks used for the determination of the various elements in the different samples have been summarized in Table 2.

### Results and Discussions

INAA method has been used to determine short-lived and medium to long-lived nuclides in crude oil, petroleum products and waste from the oil refinery in Ghana. A total of 27 elements namely Al, As, Ba, Br, Ca, Ce, Cd, Cl, Co, Cr, Cu, Fe, Ga, Hg, K, La, Mg, Mn, Na, Ni, S, Sc, Th, Ti, U, V, and Zn were

determined and analysed for 14 different petroleum samples using INAA technique.

The sensitivity of the method used in this work was confirmed by the good agreement between the obtained values and the certified values for NIST SRMs as shown in Table 1. The accuracy and precision of the INAA scheme used in this work (irradiation scheme for the determination of the radionuclides and the nuclear data used as shown in Table 2) were validated by the analysis of 10ppm and 20ppm NIST single standards elements under the same experimental conditions as the samples.

Table 3 shows the physical characteristics of the crude oils, products and residual oils. It can be seen that coco crude blend has the highest density with end boiling point (EBP) of 181 and the highest viscosity of 480. The crude with the lowest density is the brass river with EBP of 176 and viscosity of 143.

### Crude Oil

Multi – trace elemental concentrations for four crude oil blends from the Tema Oil Refinery analysed by INAA in this work are presented in Table 4. In all the four crude oil blends, measureable concentrations of Al, As, Ba, Br, Ca, Cd, Cl, Co, Cr, Cu, Fe, Ga, Hg, K, La, Mg, Mn, Na, Ni, Th, U, V, and Zn were found. Generally, the data shows that, the trace metal content increased on proceeding from a light to heavy crude oil blend. It can be seen from the results that the metal content of crude oil varied with geographical location of crude oil source. The nature of these metals and their abundance in crude oils provide information on the origin, migration and maturation of petroleum as well as indicating the regional geochemical prospecting base [2,8-10]. As a rule, the metal contents increase with asphaltic contents of the crude oils (i.e the heavier the crude oil the higher its metal contents and vice versa [11].

Figure 1 presents the V/Ni ratios of the different crude oil blends. The V/Ni ratio is a good parameter for differentiating crude oils from various locations [12,13]. The results obtained in this study confirm and show that the ratio increases from light to heavy crude oils.

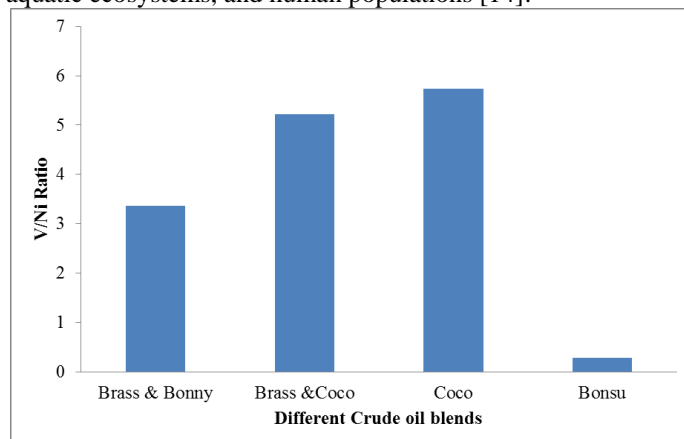
Concentration of metals in crude oils can be used to classify oils into families. Low V/Ni ratios (<0.5) are expected for petroleum derived from marine organic matter, with high to moderate sulphur content, while V/Ni ratios (1–10) are expected for petroleum derived from lacustrine and terrestrial organic matter [9]. Oils from marine organic matter have high concentrations of metals (particularly Ni and V). This is expected since for marine source rocks, there is an abundant input of porphyrin-precursor chlorophylls to the organic matter derived from algae and bacteria [9]. 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.

Concentration levels recorded for volatile elements like Cl, Br, and S were low with the total Sulfur level obtained for all crude oil blends used in this study found to be within the globally accepted range (0.1–0.5% wt) for sweet crude oil [14].

Since the S levels for both crude oils fall within acceptable limits, the environmental and human health impact will be significantly less compared to other crude oils reported with high S content from countries, like Venezuela, Canada, Saudi Arabia, Kuwait, Iran, China, and Libya [2,15,16].

Combustion of high sulphur containing crude oil generates dangerous levels of sulphur dioxide (SO<sub>2</sub>) with severe environmental and human health effects. SO<sub>2</sub> has respiratory impacts, such as lung irritation, increased breathing rates, and

suffocation. The most serious health effect is the aggravation of asthma and chronic bronchitis. SO<sub>2</sub> can also irritate the throat and eyes. It contributes to the formation of acid rain, which may cause extensive damage to materials and terrestrial ecosystems, aquatic ecosystems, and human populations [14].



**Fig 1: Graph showing the V/Ni ratio for the various crude oil blends.**

Knowledge of the constituents of crude oil to be processed is very important to the refinery in order to know the level of contaminants in crude oil before desalting and after desalting to help plan desalting and chemical injections. Effective desalting will help reduce scaling in equipment, reduction in corrosion especially at the crude column overhead lines and to obtain good quality residue which serves as a feed to the RFCC Unit. Ca and Mg can form salts or soaps with carboxylic acids. These compounds act as emulsifiers, and their presence is undesirable. When crude oil is processed, sodium and magnesium chlorides produce hydrochloric acid, which is very corrosive.

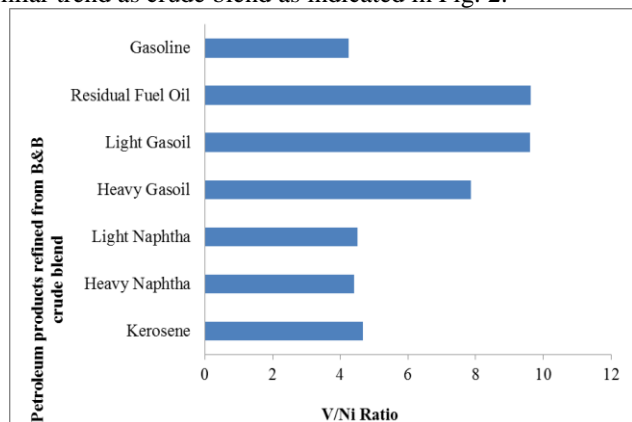
Most heavy metal emissions are the result of industrial activity, and one of the identified potential sources is the oil industry; either directly through stack emissions from refineries or indirectly from emissions resulting from combustion of hydrocarbon fuels. In order to assess the magnitude of metal emission by the oil industry it is necessary to have an accurate knowledge of the metal content of the crudes which the industry processes.

The metal content of crude oil from Nigerian oilfields in literature shows a wide variation as shown in Table 6. For example, from Table 6, Udo et al., 1992 [17] reported V content in the range of 3.7- 40.0 ppm; Nwachukwu et al., 1995 [18] reported 0.01 – 1.83; Oluwole et al., 1993 [19] reported 0.54 – 1.20; Akinlua et al., 2007 [20] reported 0.011 – 0.029 ppm; Odebumi and Adeniyi 2004 [21] also observed 0.48-4.25 ppm, while this work which used some crude oil from Nigeria gave values in the range 1.45-7.94 ppm. The wide variation may be possibly due to a combination of several factors including the source of the crude, sample handling procedures and different analytical techniques used.

The results were compared with data from other countries as shown in Table 7. The metal content compare well with data from other countries around the world. Despite the low metal content in crude oil blends observed in this study compared with others in most cases as seen from Table 7, the low levels, in crude oil blends especially Na, Ca, Mg, V, Fe and Ni are high enough to cause corrosion of turbines, distillation columns, etc and poisoning of catalyst used in cracking and reforming process at the refinery and hence their presence is still harmful and should be removed.

### Petroleum Products and Residual Fuel Oil

Table 5 presents a summary of the mean concentrations of trace constituents in four petroleum products, residue and gasoline refined from a fluid catalytic cracking processing of the residue all from the Brass and Bonny crude oil blend. Similar trend of increasing trace metal content with asphaltic contents was also observed for petroleum in this study. In general metal content in heavier products were higher than those in lighter products. V/Ni ratio for petroleum products also showed a similar trend as crude blend as indicated in Fig. 2.



**Fig 2: Graph showing the V/Ni ratio for the various petroleum products from B&B crude oil blend**

The metal contents of Nigerian petroleum products are in general lower than those of petroleum products from other regions of the world. The report of Adolfo et al., 2007[22], for example show iron contents of 12.39ppm, 725 mg/kg and 113.2 ppm for petroleum products from Central American Region (USA), Mexico and Venezuela respectively. However, even as this low levels, the metal contents of Nigerian petroleum products, and especially of Na, Ca, V, Ni, Cu and Fe is high enough to cause corrosion of turbines, distillation towers and the presence of this contaminants in the charging stock (RFO) for catalytic cracking affects the activity of the catalyst and result in increased gas and coke formation and reduced yield of gasoline.

The data in Table 5 also shows that the weight percentage of total sulphur in various petroleum products, fall within the range for sulphur expected in Nigerian crude oils and petroleum products, i.e. 0.05 – 0.30 wt/% [23-25]. It can be deduced from Table 2 that Gasoline, (light ends fraction), Kerosene (Intermediate fraction), Heavy Gasoil & Light Gasoil (Diesel fuel) (Distillates) and Residual fuel (heavy distillates) contain 0.03, 0.04, 0.08 & 0.07 and 0.29 W/% sulphur respectively. The presence of metallic elements in gasoline, especially those which have suspected biological toxicity such as Ce, As, V, Ni, and Cr are of concern to environmentalists because of the potential widespread dissemination of these constituents, most in the respirable range, at ground level [26].

Several studies of the particle size of trace metal components in ambient air have shown that Pb, V, and Zn are associated with particles predominantly of a submicron aerodynamic size [27,28]. Particles in this size range can remain suspended in air for long periods of time and can penetrate deep into the human respiratory system[29] (Morrow 1964). Furthermore, many of the metals found in gasoline, notably Fe and Pb[30], can act as catalysts in the transformation of primary atmospheric pollutants to secondary pollutants, e.g., SO<sub>2</sub> to SO<sub>4</sub>.

Although, gasoline combustion may not necessarily be the major source of these constituents, the fact that over several thousand billion gallons are consumed annually indicates that

gasoline combustion should be considered in estimates of environmental emissions of these metals. Also, when fuels are combusted, metals present in the fuels can form low melting compounds that are corrosive to metal parts. Another environmental concern, mentioned earlier is the presence of constituents such as S, which may poison exhaust catalytic devices thereby reducing their efficiency and effective operating life.

Coupled with this concern is the distinct possibility that fine metal particles may be produced from the exhaust catalysts themselves as recently reported by Balgord (1973) [31]. There is also concern that S in gasoline may be emitted as sulfuric acid mist after oxidation by catalytic devices. It becomes important to characterize the trace constituents in the fuel in order to assess the amount of trace metals emitted by exhaust catalytic devices.

Although the results generally obtained for the petroleum products in this work were lower compared with other available global data, however, the results from this study is enough to contribute significantly to atmospheric pollution. Hence, it may be necessary for National Regulatory Authorities to institute some type of control at the refinery or distributor outlet to remove or reduce further trace contaminants from fuel before it is use in motor vehicles.

### Sludge, Scale and Residual Mud Water

The results of the waste petroleum samples comprising of sludge, scale and residual mud water are represented in Table 6. The data showed measurable amounts of Al, As, Ba, Br, Ca, Ce, Cd, Cl, Co, Cr, Cu, Fe, Ga, Hg, K, La, Mg, Mn, Na, Ni, S, Sc, Th, Ti, U, V, and Zn for the samples. From Table 6, it is clear that metal contents increase in the order of Residual mud water < Sludge < Scale. The results of metal content in waste from this study compares well with data from other work conducted in other refinery waste[32].

Based on the results obtained and the analytical procedure used in this work, it can also be seen that, the metal contaminants found in the petroleum products and waste are native to the crude oil and its origin. Generally metal contents were higher in waste samples followed by crude oil and petroleum products.

### Conclusion

A nuclear analytical technique (INAA) has been used to characterize metal contaminants in crude oil, petroleum products and waste from the Tema oil refinery.

In all a total of 27 trace elements were determined from the analyses of 14 different petroleum samples. The INAA technique has shown from this study to be very feasible in the analysis of these volatile petroleum samples and this will complement the conventional techniques used at the refinery and to achieve results in terms of product quality, corrosion control, preservation of RFCC catalyst at the Tema oil refinery and provide accurate data on emission estimate resulting from either directly through stack emissions from refinery or indirectly from emissions of combustion of hydrocarbons.

Generally, metal contents were higher in waste samples followed by crude oil and petroleum products. Although, results obtained for petroleum products in this work were generally lower compared with other available global data, it is important that control measures are instituted by National Regulatory Authorities since these could cause a lot of problems to the end user especially in motor vehicles.

From the results obtained for sludge and scale samples, appropriate treatment strategy need to be adopted to reduce or remove these contaminants.

**Table 1: Analysis of standard reference material by INAA (NIST, Single standard elements 20ppm and IAEA-SOIL-7 (mg/kg) used for the Validation)**

Elements	NIST SRM 20ppm		IAEA-SOIL-7 (mg/kg)	
	Measured value (ppm)	Certified value (ppm)	Measured value ( mg/kg )	Certified value ( mg/kg )
Al	19.56	20ppm	4702	4700
Mn	21.05	20ppm	630	631
Mg	20.03	20ppm		
V	20.14	20ppm	66	66
Cu	20.02	20ppm		
Ca	19.76	20ppm	162998	163000
Hg	18.98	20ppm	0.03	0.04
As	19.57	20ppm	13.2	13.4
K	20.36	20ppm	12103	12100
Na	20.17	20ppm		
S	19.83	20ppm		
Fe	20.10	20ppm	25701	25700
Co	18.95	20ppm	8.7	8.9
Cr	18.63	20ppm	59.2	60

**Table 2: Nuclear data of elements used in analysis of crude oil, petroleum products and waste**

Element	Radioisotope	Energy(keV)	Half-Life	Irradiation time	Counting time
Aluminium (Al)	<sup>28</sup> Al	1778.97	2.24min	3min/10s	10min
Arsenic (As)	<sup>76</sup> As	559.1	1.08d	1h	2h
Barium (Ba)	<sup>131</sup> Ba	496.3	11.5d	1h	2h
Bromine (Br)	<sup>82</sup> Br	776.5	35.3h	1h	2h
Calcium (Ca)	<sup>49</sup> Ca	3084.4	8.72min	3min/10s	10min
Cadmium (Cd)	<sup>115m</sup> In	336.2	53.5h	1h	2h
Chlorine (Cl)	<sup>38</sup> Cl	1642.7	37.24min	3min/10s	10min
Cobalt (Co)	<sup>60</sup> Co	1332.5	5.27y	1h	2h
Chromium (Cr)	<sup>51</sup> Cr	320.08	27.7d	1h	2h
Copper (Cu)	<sup>66</sup> Cu	1039.23	5.12m	3min/10s	10min
Iron(Fe)	<sup>59</sup> Fe	1099.25	44.5d	1h	2h
Gallium (Ga)	<sup>72</sup> Ga	834.01	14.1h	1h	2h
Mercury (Hg)	<sup>197</sup> Hg	77.4	64.1h	1h	2h
Potassium (K)	<sup>42</sup> K	1524.7	12.36h	1h	2h
Lanthanum (La)	<sup>140</sup> La	328.8 1596.2	40.23 h	1h	2h
Magnesium (Mg)	<sup>27</sup> Mg	1014.4	9.46m	3min/10s	10min
Manganese (Mn)	<sup>56</sup> Mn	1810.7	2.58h	3min/10s	10min
Sodium (Na)	<sup>24</sup> Na	2754.01	14.96h	1h	2h
Sulphur (S)	<sup>27</sup> S	3102.4	5.06min	3min/10s	10min
Nickel(Ni)	<sup>59</sup> Ni	810.8	70.9d	1h	2h
Thorium (Th)	<sup>233</sup> Pa	312.17	27.0d	1h	2h
Titanium (Ti)	<sup>51</sup> Ti	320.1	5.8min	3min/10s	10min
Uranium (U)	<sup>239</sup> Np	277.6	2.35d	1h	2h
Vanadium (V)	<sup>52</sup> V	1434.1	3.74min	3min/10s	10min
Zinc (Zn)	<sup>65</sup> Zn	1115.55	244.26d	1h	2h

**Table 3: Physical Characteristics of Crude Oils, Products and Residual Fuel Oil**

Fraction & Property	Crude oil, Products and Residue				Specification
	Bonny Light	Brass River	Coco	Bonsu	
Whole Crude Oil					
API	34.7	41.1	31.4	35.1	
Pour Point °C	+3	0	+27	-3	
Sulphur %wt	0.11	0.07	0.11	0.17	
Density	850.9	819.3	868.1	848.7	
TAN	0.21	0.30	0.34	0.17	0.33
Light Naphtha					
RVP	0.58	0.56	0.57		0.65
Heavy Naphtha					
EBP °C	177	176	181		190
Kerosene					
TAN	0.012	0.014	0.045		0.015
Gas Oil					
Pour Point °C	+6	+9	+12		+15
Residual Fuel Oil					
CCR	3.6	2.2	8.0		3.8
Sulphur	0.32	0.24	0.29		0.33
Viscosity	60	143	480		371

API, American Petroleum Institute; TAN, Total Acid Number; RVP, Reid Vapour Pressure; EBP, End Boiling Point; CCR, Coracin Carbon Ratio

Table 4: Calculated metal concentrations in the different crude oil blends

Elements	Concentration ( ppm)				
	*Brass & Bonny(B&B)	*Brass & Coco (B&C)	*Coco	**Bonsu	Mean ± STDEV
Al	2.62 ± 0.24	3.20 ± 0.20	3.70 ± 0.12	2.30 ± 0.10	2.96 ± 0.62
As	0.22 ± 0.001	0.42 ± 0.04	0.33 ± 0.06	0.52 ± 0.03	0.37 ± 0.12
Ba	0.06 ± 0.001	0.08 ± 0.001	0.10 ± 0.001	0.04 ± 0.001	0.07 ± 0.03
Br	0.15 ± 0.02	2.80 ± 0.20	2.30 ± 0.12	1.42 ± 0.14	1.67 ± 1.16
Ca	0.07 ± 0.001	0.09 ± 0.001	0.05 ± 0.001	1.04 ± 0.001	0.31 ± 0.48
Cd	0.003 ± 0.0001	0.002 ± 0.0003	0.0015 ± 0.0001	0.0012 ± 0.0001	0.002 ± 0.001
Cl	10.42 ± 0.12	15.21 ± 0.08	13.24 ± 0.20	12.91 ± 0.05	12.95 ± 1.97
Co	0.24 ± 0.001	0.59 ± 0.001	0.47 ± 0.001	1.08 ± 0.001	0.60 ± 0.35
Cr	0.03 ± 0.001	0.14 ± 0.01	0.12 ± 0.01	0.10 ± 0.01	0.10 ± 0.05
Cu	1.35 ± 0.01	1.64 ± 0.04	1.55 ± 0.03	0.27 ± 0.02	1.20 ± 0.63
Fe	1.80 ± 0.01	4.60 ± 0.15	3.80 ± 0.12	4.93 ± 0.24	3.78 ± 1.40
Ga	0.002 ± 0.0004	0.11 ± 0.005	0.09 ± 0.003	0.1 ± 0.002	0.08 ± 0.05
Hg	0.001 ± 0.0003	0.009 ± 0.001	0.006 ± 0.001	0.008 ± 0.001	0.01 ± 0.004
K	0.09 ± 0.01	0.10 ± 0.02	0.09 ± 0.02	0.07 ± 0.03	0.09 ± 0.013
La	0.08 ± 0.001	0.16 ± 0.03	0.12 ± 0.03	0.2 ± 0.05	0.14 ± 0.05
Mg	1.15 ± 0.02	1.52 ± 0.02	1.41 ± 0.02	1.21 ± 0.10	1.32 ± 0.17
Mn	0.31 ± 0.01	0.41 ± 0.04	0.33 ± 0.02	0.06 ± 0.01	0.28 ± 0.15
Na	64 ± 1	136 ± 3	141 ± 3	97 ± 1	110 ± 36
Ni	0.58 ± 0.01	1.52 ± 0.05	1.36 ± 0.05	12.0 ± 0.2	3.87 ± 5.44
S (%)	0.10 ± 0.001	0.13 ± 0.001	0.12 ± 0.02	0.18 ± 0.01	0.13 ± 0.03
Th	2.43 ± 0.4	2.65 ± 0.5	2.6 ± 0.4	3.1 ± 0.8	2.70 ± 0.28
U	0.3 ± 0.02	0.28 ± 0.04	0.3 ± 0.05	0.72 ± 0.1	0.40 ± 0.21
V	1.95 ± 0.01	7.94 ± 0.32	7.80 ± 0.05	3.4 ± 0.02	5.27 ± 3.06
Zn	0.88 ± 0.02	1.90 ± 0.03	1.84 ± 0.05	0.45 ± 0.02	1.27 ± 0.72

(\*\*) – Crude oil from Ghana; (\*) – Crude oil from Nigeria

Table 5: Trace elements concentration in petroleum products refined from B&amp;B crude blend

Elements	Concentration (ppm)						
	Kerosene	Heavy Naphtha	Light Naphtha	Heavy Gasoil	Light Gasoil	Residual Fuel Oil	Gasoline
Al	0.03 ± 0.001	0.04 ± 0.001	0.02 ± 0.001	0.08 ± 0.002	0.05 ± 0.005	0.27 ± 0.03	0.02 ± 0.001
As	0.003 ± 0.001	0.003 ± 0.001	0.003 ± 0.001	0.008 ± 0.001	0.007 ± 0.001	0.24 ± 0.02	0.002 ± 0.0004
Ba	0.03 ± 0.001	0.03 ± 0.001	0.02 ± 0.001	0.05 ± 0.001	0.04 ± 0.001	0.12 ± 0.01	0.02 ± 0.001
Br	0.04 ± 0.001	0.05 ± 0.001	0.03 ± 0.001	0.07 ± 0.002	0.06 ± 0.002	0.14 ± 0.02	0.03 ± 0.001
Ca	0.14 ± 0.01	0.15 ± 0.01	0.09 ± 0.001	0.27 ± 0.001	0.24 ± 0.001	1.09 ± 0.01	0.09 ± 0.001
Cl	0.36 ± 0.01	0.37 ± 0.02	0.23 ± 0.01	0.49 ± 0.03	0.46 ± 0.02	0.75 ± 0.01	0.22 ± 0.01
Co	0.04 ± 0.001	0.05 ± 0.001	0.03 ± 0.001	0.11 ± 0.01	0.09 ± 0.01	0.54 ± 0.01	0.03 ± 0.001
Cr	0.03 ± 0.001	0.06 ± 0.002	0.01 ± 0.001	0.05 ± 0.001	0.04 ± 0.001	0.08 ± 0.001	0.01 ± 0.001
Cu	0.34 ± 0.01	0.36 ± 0.001	0.20 ± 0.002	0.66 ± 0.001	0.54 ± 0.001	1.22 ± 0.04	0.22 ± 0.002
Fe	1.14 ± 0.02	1.13 ± 0.04	1.01 ± 0.03	1.38 ± 0.05	1.28 ± 0.03	3.30 ± 0.01	1.02 ± 0.03
K	0.03 ± 0.001	0.03 ± 0.001	0.02 ± 0.001	0.04 ± 0.001	0.03 ± 0.01	0.08 ± 0.002	0.02 ± 0.001
La	0.03 ± 0.001	0.02 ± 0.001	0.02 ± 0.001	0.04 ± 0.001	0.03 ± 0.001	0.07 ± 0.006	0.02 ± 0.001
Mg	0.48 ± 0.02	0.50 ± 0.01	0.41 ± 0.02	0.82 ± 0.02	0.78 ± 0.02	2.14 ± 0.04	0.42 ± 0.02
Mn	0.18 ± 0.01	0.21 ± 0.01	0.14 ± 0.001	0.32 ± 0.02	0.30 ± 0.01	0.92 ± 0.05	0.14 ± 0.001
Na	0.21 ± 0.05	0.22 ± 0.01	0.16 ± 0.01	0.38 ± 0.06	0.33 ± 0.01	0.44 ± 0.02	0.15 ± 0.01
Ni	0.04 ± 0.002	0.04 ± 0.001	0.03 ± 0.001	0.07 ± 0.001	0.05 ± 0.001	0.22 ± 0.04	0.03 ± 0.001
S (%)	0.04 ± 0.001	0.05 ± 0.001	0.03 ± 0.001	0.08 ± 0.001	0.07 ± 0.001	0.29 ± 0.01	0.03 ± 0.001
V	0.17 ± 0.01	0.16 ± 0.01	0.15 ± 0.01	0.55 ± 0.04	0.48 ± 0.01	2.12 ± 0.05	0.14 ± 0.01
Zn	0.24 ± 0.01	0.22 ± 0.01	0.19 ± 0.01	0.48 ± 0.02	0.43 ± 0.02	0.92 ± 0.02	0.18 ± 0.01

Table 6: Comparison of range of metal content (ppm) in Nigerian crude oil used in this work with other available data on crude oil from Nigerian oilfields

Trace Elements	Akinlua et al., 2007	Nwachukwu et al., 1995	Oluwole et al., 1993	Udo et al., 1992	Odebunmi et al., 2004	This work
Co	0.001 – 0.032	0.003 – 1.17	0.01 – 0.99	0.46 - 3.54		0.24 – 0.59
Cr	0.006 – 0.024	0.02 – 0.22	0.03 – 0.13	0.30 - 0.70	0.01 - 0.16	0.03 – 0.14
Cu	0.003 – 0.019	0.54 – 42.31	1.86 – 18.9	0.03 - 0.07		1.35 – 1.64
Fe	0.011 – 1.241	0.006 – 25.07	3.40 – 9.54	0.06 - 0.36	0.27 - 0.42	1.80 – 4.60
Ni	0.026 – 0.144	0.35 – 11.28	0.54 – 5.71	4.40 - 6.90	0.13 - 0.26	0.58 – 1.52
V	0.011 – 0.029	0.01 – 1.83	0.54 – 1.20	3.70 - 40.0	0.48 - 4.25	1.95 – 7.94

**Table 7: Comparison of crude oil data in this present work with available global data**

Trace Elements	USA <sup>a</sup>	Libya <sup>a</sup>	Venezuela <sup>a</sup>	Canada <sup>a</sup>	Columbia <sup>b</sup>	East indies <sup>b</sup>	Middle East <sup>b</sup>	Sudan <sup>c</sup>	China <sup>d</sup>	Ghana <sup>e</sup>	Ghana This work
Al	0.3		1.0		0.3	6.0	7.0		46.4	2.71	2.96
As	0.655	0.077	0.284	0.111					0.31	0.68	0.37
Ba									92.7		0.07
Br	0.29	1.33		0.491					19.6	1.14	1.67
Ca	1.6					1.9		1.53		1.21	0.31
Cd	0.004							0.144			0.002
Cl	1.47	1.81		39.3					1000	14.3	12.95
Co	13.5	0.032	0.178	0.054		1.9		0.85	0.65	2.86	0.60
Cr	0.640	0.0023	0.430	0.093		0.2	0.1		2.17		0.10
Cu	0.93	0.19	0.21		7.0	1.0	5.0	1.39	7.18	0.29	1.20
Fe	68.9	4.94	4.77	10.8	0.4	61.0	5.0	3.00	194	5.88	3.78
Ga	0.30	0.01									0.08
Hg	23.1		0.027	0.084							0.01
K	2.9	4.93	2.1				0.7			0.79	0.09
La									0.26		0.14
Mg	2.0		1.7		1.2	1.7	7.0	0.40		1.15	1.32
Mn	1.20	0.79	0.21	0.048				0.42	5.89	0.05	0.28
Na	13.2	13.0	20.3	3.62	9.4	15.0	0.5	28.36	891	101	110
Ni	98.4	49.1	117	9.38	10	1.0	30	3.71	63.6	12.6	3.87
S	9.90	4694		1450					4082	1940	1300
Th											0.17
U		0.015									2.70
V	7.5	8.2	11.10	13.6	72		100		10.4	3.71	0.40
Zn	9.76	62.9	0.692	0.670		0.6	2.0	0.99	5.83	0.38	5.27

<sup>a</sup>Filby and shah 1975; Hitchon etal 1975; Williams and Cawley 1963<sup>b</sup>Williams and Cawley 1963<sup>c</sup>Elsamoual 2001<sup>d</sup>Chifang et al 1991<sup>e</sup>Appenteng etal 2012**Table 8: Trace elements concentration in Scale, Sludge, Residual mud water and waste water from the refinery**

Elements	Concentrations		
	Scale (%wt)	Sludge (%wt)	Residual mud water (ppm)
Al	0.08 ± 0.002	0.52 ± 0.01	1.95 ± 0.20
As	0.003 ± 0.0001	0.001 ± 0.0001	0.15 ± 0.01
Ba	0.03 ± 0.001	0.03 ± 0.001	0.05 ± 0.001
Br	0.06 ± 0.002	0.13 ± 0.02	0.25 ± 0.04
Ca	1.74 ± 0.01	4.32 ± 0.05	0.07 ± 0.001
Ce	0.03 ± 0.001	0.03 ± 0.001	
Cl	0.09 ± 0.001	0.07 ± 0.002	8.50 ± 0.05
Co	0.003 ± 0.0001	0.009 ± 0.001	0.19 ± 0.01
Cr	0.003 ± 0.0001	0.05 ± 0.002	0.02 ± 0.001
Cu	4.50 ± 0.25	2.12 ± 0.03	0.62 ± 0.01
Fe	74.2 ± 3.5	49.3 ± 1.1	0.94 ± 0.01
Ga	0.01 ± 0.001	0.02 ± 0.001	0.002 ± 0.0002
K	0.13 ± 0.006	0.35 ± 0.02	0.12 ± 0.01
La	0.08 ± 0.01	0.15 ± 0.02	0.09 ± 0.001
Mg	0.11 ± 0.002	0.25 ± 0.01	0.38 ± 0.01
Mn	0.41 ± 0.02	0.36 ± 0.02	0.15 ± 0.001
Na	0.02 ± 0.001	0.07 ± 0.001	45 ± 0.8
Ni	0.85 ± 0.01	0.09 ± 0.002	0.24 ± 0.001
S	1.15 ± 0.03	3.60 ± 0.21	
Sc	0.35 ± 0.01	2.13 ± 0.04	
Ti	0.05 ± 0.001	1.11 ± 0.002	
Th	0.001 ± 0.0001	0.001 ± 0.0001	2.33 ± 0.4
U	0.0003 ± 0.00001	0.0002 ± 0.00001	0.3 ± 0.01
V	0.005 ± 0.0001	0.008 ± 0.001	0.98 ± 0.01
Zn	0.005 ± 0.0001	0.06 ± 0.002	0.25 ± 0.01

Regular monitoring prior to disposal may be necessary to ensure occupational and public safety as well as the environment.

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