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Metallic Composition Analysis of Crude Petroleum from Some Oil Fields in Ghana

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

Qualitative and quantitative analyses of chemical elements in crude petroleum using energy-dispersive X-ray fluorescence spectroscopic technique has attracted the attention of scientific world because it is fast, cheap, non-destructive and assurance in quality compared to other methods. Metallic element characterisation of crude petroleum is important in the petrochemical industry because it determines rock reservoir properties, the technology needed for extraction and refinery process, hence an exciting field that calls for research. X-ray fluorescence method was used for metallic composition analysis of four rundown crude petroleum samples (SB-2, SB-4, TB-2 and TB-1) from three oil fields (Saltpond, TEN and Jubilee). It was conducted at the National Nuclear Research Institute of Ghana. Analysis of the four samples concluded that oil field maturity decreases orderly from Saltpond, Jubilee and TEN. Vanadium-nickel ratios for each crude petroleum sample was less than 0.5, indicating that both Saltpond and Tano sedimentary rocks are of marine organic origin. Higher concentration levels of rare earth metal elements (scandium and yttrium) in the Saltpond sedimentary basin compared to Tano sedimentary rock suggest seismic effect of McCarthy Hills on Saltpond Basin. The strong negative correlation between the vanadium-nickel ratio (predictor) and scandium concentration (dependent) among the three oil fields implies that scandium concentration can equally be used to characterise the oil fields just as the vanadium-nickel ratios.

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1. INTRODUCTION

Crude petroleum is a naturally occurring yellow-to-black liquid found in geological formations in rock sediment beneath the Earth's surface [1]. It can be acquired from an extensive range of different geological sources [1,2]. Crude petroleum contains variety of complex metallic ions that characterise its geological composition and therefore, the oil field [1,2,3]. These metallic ions depict properties such as maturity, geochemical hydrocarbon flow direction, origination, thermal catalytic effect, metal composition of the oil fields and its rock sediment [1,2,5].

For sedimentation of organic matter to form rock reservoir, many metal elements in traces are incorporated and intrinsically embedded [5]. These metal elements present in the crude petroleum are mostly porphyrins and non-porphyrins of nickel, iron, zinc and vanadium [1,2,4,6]. They are acquired from accumulations of chlorophylls of algae and phytoplankton, mostly present in the environments of marine organic deposit [2,6,7]. However, depositional environments through plant chlorophylls accumulation indicates a terrestrial origin of crude petroleum [4,6,7].

The quality assessment of metal ions in crude petroleum has environmental and industrial importance. The metallic composition data from crude petroleum sample of an oil field determines the technology for oil field development, refinery processes, ecological lives protection measures and quality level of the crude [1]. For instance, vanadium and nickel metal elements in crude petroleum have received the attention of investigators because they are found in higher concentrations [8,9]. Their presence may cause undesirable effect by poisoning the hydrogenation catalyst used during thermal cracking process of crude petroleum [1,8]. Heavy metals in petroleum pollutes the environment during exploration, production and refinery process when exposed [1,10,11]. Heavy metals ions such as lead, arsenic, mercury, chromium, cadmium and thallium, in crude petroleum, are toxic to lives [1,10,12] and may harm both aquatic and terrestrial ecological equilibrium [1,11,13,14]. Therefore, it is important to conduct comprehensible impact assessment on potentially hazardous and thermal catalytic effect trace metal elements in crude petroleum for environmental safety and effective productivity technique [1].

Vanadium-nickel ratio is an accepted tool for oil field characterisation for maturity, origin, hydrocarbon flow direction and field correlation [1,2,15]. The physical and geochemical changes in properties of an environment determines the maturity of sedimentary rock basin and oil field [1, 4, 15], and this is manifested in vanadium-nickel ratio [4, 9, 15]. According to previous studies, lesser values of V/Ni and V/(Ni+V) ratios suggest an increase in the maturity of crude petroleum rock basins and oil fields [1, 5]. If V/Ni ratio is < 0.5, it suggests marine organic matter origin [4, 16]; and V/Ni ratio > 0.5 suggest lacustrine and terrestrial organic matter origin [5, 16].

Rare earth elements are found in the upper mantle of the earth and their presence in sedimentary rocks suggest the effect of physical activity of the Earth's mantle on crust where a sedimentary rock is located [17]. The relative abundance and pattern of rare earth metal can be used as a tool for hydrocarbon-geochemical tracer [6, 18]. The concentration of rare earth element can be employed for crude petroleum classification and suggested that their pattern in crude petroleum can provide genetic information [5, 18, 19].

Ghana now has discovered four main sedimentary rock basins, namely: Saltpond Basin (Central Basin), Tano-Cape Three Point Basin (Western Basin), Accra-Keta Basin (Eastern Basin) and Voltaian Basin [20, 19]. Tano-Cape Three Point Basin is currently productive, while Accra-Keta and Voltaian Basins are under study for economic production viability [19, 21]. Currently, Saltpond Basin has stopped production because of economic reasons [21]. Fig. 1 is a map describing the topography of the sedimentary rocks along the coast of Ghana in the Gulf of Guinea.

Developing scientific methods and procedures for determining the characteristics of various crude petroleum from different geological sources for standardisation is therefore important to the petroleum industry and calls for research. Spectroscopic techniques, mainly based on X-ray fluorescence [23,24], have gained relevance in the field of petroleum research because it provides valuable information related to the intrinsic chemical characteristics of an analysed sample [23, 25]. It is therefore important to study the metallic characteristics of Ghana's crude petroleum so as to obtain a comprehensive data for the future development of petroleum industry and metal extraction technology. This research study will create an opportunity for petroleum stakeholders to properly invest in crude production, refinery and metal extraction techniques. X-ray emission properties such as intensity, energy state, wavelength and frequency are strongly influenced by the chemical composition and physical characteristics of crude petroleum [23,25]. Energy-dispersive X-ray fluorescence (EDXRF) spectroscopy offers high sensitivity and gives better detection techniques [23]. For these reasons, EDXRF techniques is currently used widely in the petroleum industry for crude analysis. Fig. 2 is the schematic representation of the EDXRF system. The spectrograph represents the characteristic energy states of the elements in the liquid sample and their coresponding fluorescence intensities on the computer screen.

In this paper, qualitative elemental identification and quantitative estimation based on energy dispersive X-ray fluorescence spectral data from crude petroleum samples from Ghana are reported. Estimation of vanadium-nickel ratio for each crude sample and prediction of oil field's maturity was another interest of the study. Also, the study employed energy dispersive X-ray fluorescence technique to identify geochemical disparity between the Saltpond and Tano sedimentary basins. Concentration levels of heavy metal elements in the crude petroleum samples that may cause ecological imbalance when exposed were considered. Lastly, the study aimed to compare vanadium-nickel ratio of the oil fields to sulphur, and scandium concentrations to identify the correlation among them.

Fig. 2 is the diagrammatic representation of energy dispersive X-ray system. From the diagram, the red rays represent the primary X-rays from the anode of the tube to the liquid sample for absorption and excitation. The blue rays are the secondary X-rays emitted by the atoms of the elements in the liquid sample upon de-excitation. The black rays are the electric pulses from the silicon drift detector, amplifiers and spectrometer. On the computer screen, the spetrograph represents the characteristic energy states of the elements in the liquid sample and their coresponding intensities.

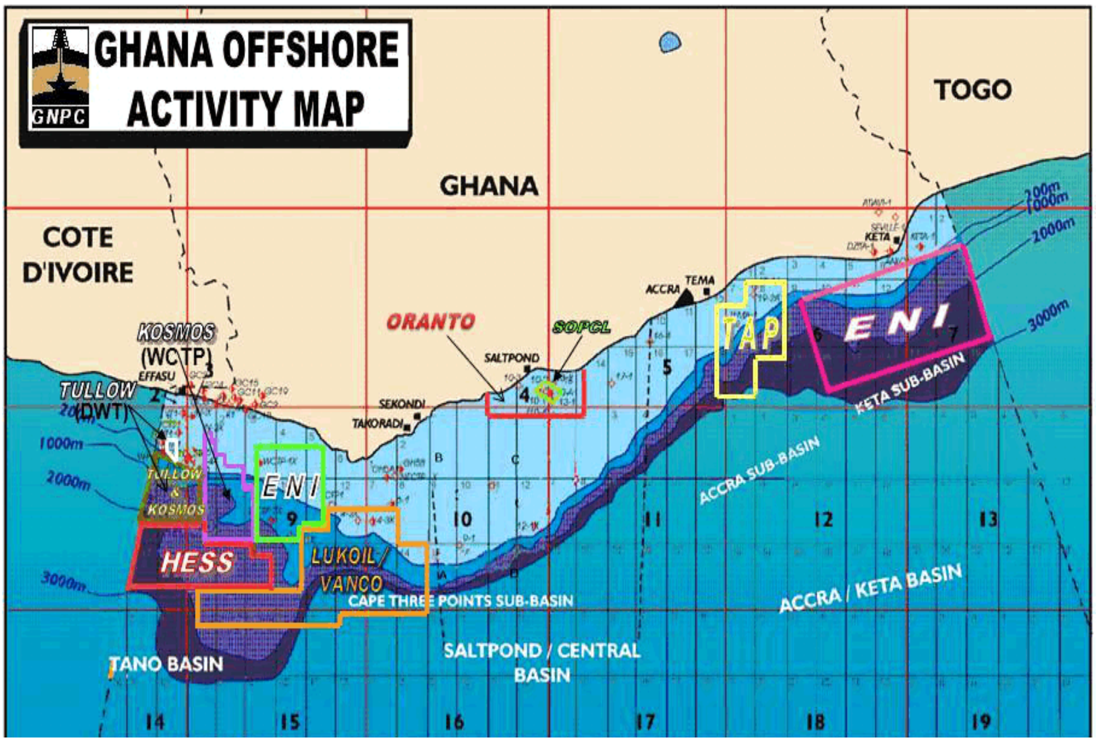

Fig. 1. The topography of tano, saltpond and accra-keta sedimentary basins of Ghana [22]

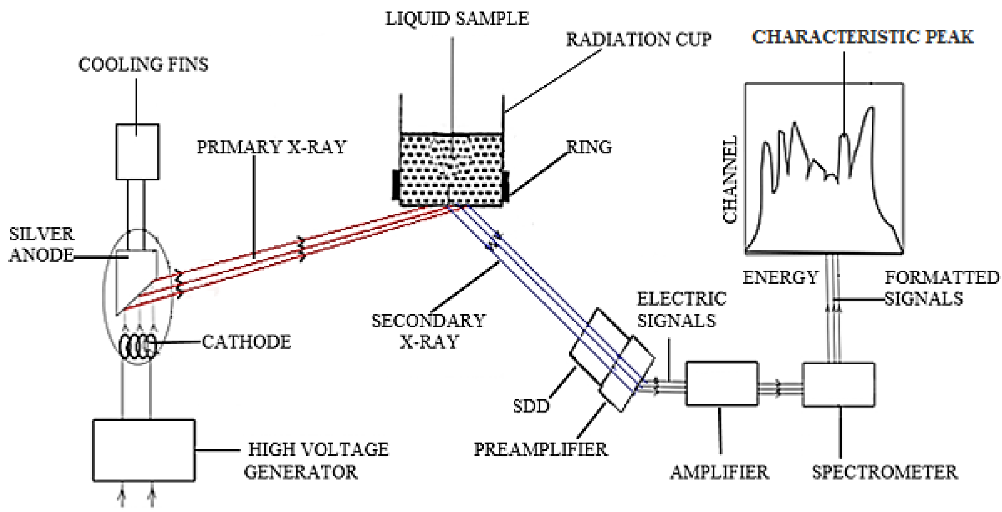

Fig. 2. Diagrammatic representation of energy dispersive X-ray fluorescence system

2. MATERIALS AND METHODS

2.1 Samples

SB-2 and SB-4 are crude petroleum samples obtained from the Research and Development Department of Saltpond Offshore Producing Company Limited. It is light crude oil with American Petroleum Institute (API) value of 35.1^{o}, and specific gravity of 0.8493 at 15.0 ^{0} C [26]. A total volume of 2.0 litres each of rundown crude petroleum from oil Well-2 and Well-4 of Saltpond Oil Field were obtained for this work.

TB-1 is light crude acquired from the Jubilee Oil Field of Ghana with API value of 37.41^{o} at 15.0 ^{0} C, and specific gravity of 0.8377 [27]. 2.0 litres of composite rundown crude petroleum (47th lift from FPSO MV21 Kwame Nkrumah) was acquired for this study from Tullow Ghana Limited through Gnana National Petroleum Cooperation. Jubilee Oil Field is in the Western Region of Ghana, 60.0 km offshore between Deepwater Tano and West Cape Three Points blocks off the western coast [27].

The fourth crude petroleum sample is TB-2. It was 2.0 litres rundown composite crude petroleum from TEN oil field (10th lift from FPSO MV25 Evans Atta Mills) obtained from Tullow Ghana Limited through Ghana National Petroleum Corporation. The API value of TB-2 crude is 36.2^{o} with a specific gravity of 0.8438 [28]. The TEN Oil Field is located in the Western Region of Ghana about 20.0 km west of the Jubilee Oil Field [29]. Fig. 3 shows the locations of Jubilee and TEN Oil Field in the Gulf of Guinea where samples TB-1 and TB-2 were acquired.

The samples were transported to the XRF laboratory of the Nuclear Application Centre of National Nuclear Research Institute. The crude petroleum samples were analysed using energy dispersive X-ray fluorescence spectroscopy technique. The EDXRF facility used was the AMPTEK Experimenter's Kits. It comprises of a high voltage generator, an X-ray source (Mini-X tube with Silver target), a detector (X-123 SDD), a complete X-ray spectrometer (X-123SDD, Silicon Drift Detector of 25.0 mm^{2} x 500.0 µm / 0.3 mil Be window / 1.5 Detector Extension / 2-Stage Cooler / Internal Multilayer Collimator), radiation cage (sample chamber), radiation cup and a computer.

2.2 Spectra Acquisition

The crude samples and the radiation cups were coded and 2.0 ml each was transferred into the radiation cups for the spectral analysis. The fluorescence device was set at a voltage of 45.0 kV and current of 5.0 µA and the samples irradiated for a period of 180.0 seconds each for spectra acquisition using the AMPTEK DPPMCA software. The dead-time was below 1% throughout the spectra acquisition.

The energy scale was calibrated using the characteristic peaks of Fe and Mo, and the regions of interest around these two peaks marked. The calibration dialog was opened and the energies of Fe and Mo, 6.40 keV and 17.44 keV respectively, were defined. The calibration was verified and confirmed by acquiring the spectrum of Cr which was 5.4 keV. The energy resolution of the detector was checked using the full wave at half maximum (FWHM) of Kα peak of Fe, which was slightly higher than the FWHM listed on the datasheet supplied with the detector.

The quantitative analyses of the elements in the crude petroleum (SB-2, SB-4, TB-1 and TB-2) were done using bAxil Fundamental Parameter (bAxil FP) for standard-less method. The quantitative results were purely derived from the unknown spectrum analysis based on the physical constants and parameters specified in the sample or spectrum model. The standard-less fundamental parameter calculations were completed by defining and normalizing all elemental concentrations to part per million (ppm).

3. RESULTS AND DISCUSSION

After a series of repeated computational run of the fluorescence data with fundamental parameters using liquid standards, for accuracy and precision, the certified and accepted results for elements detected and their corresponding concentration values are listed in Table 1. Individual elements in each sample with concentrations below the detection limit of the fluorescence instrument used for this study is indicated as BDL.

From Table 1, thirty (30) elements were detected and quantified based on their fluorescence intensities. On average, Saltpond Basin recorded a more significant number of elements compared to Tano Basin. Also, the values of the elemental concentrations of samples SB-2 and SB-4 from the Saltpond Basin; and TB-1 and TB-2 from the Tano Basin are not exactly the same. This suggests non-uniform geochemical distribution of the elements in the two rocks. Based on the concentration levels (< 100.0 part per million or < 0.01 weight per cent) of Fe, Cu, Co, Ni and V in Table 1, it can be stated that crude petroleum samples used for this study have relatively low content of thermal catalytic effect metal elements which is globally accepted [1, 4, 8], with probable less refinery cost [4, 31]. The average concentrations of vanadium from Tano Basin was 4.6297 times greater than that from Saltpond Basin. The distinction in the average values of vanadium concentration among the two sedimentary rock basins indicates that, geographically, Tano Basin has a broad continental shelf that supports marine aquatic life than the Saltpond Basin [32]. Also, the concentrations of nickel were observed to be in moderate quantities in each sample. These moderate values of nickel concentrations in the samples were evidence for marine plant origination since nickel occurs in traces from the ashes of aquatic plants [4].

However, considering the concentrations of Fe among the two rock basins, there was substantial disparity between them, indicating that Saltpond and Tano Basins are geochemically dissimilar [33, 34], and were formed under different geological conditions [34]. That is, geologically, Saltpond Basin is a cretaceous lacustrine rock shale [33] whilst Tano Basin is a cretaceous continental rock [35]. The concentration of Fe in the oil fields increased orderly from TEN, Jubilee and Saltpond.

Table 2 shows the concentrations of vanadium, nickel and sulphur. V/Ni and V/(Ni+V) ratios were calculated for each crude petroleum sample, and the results compared to sulphur concentrations.

The variation in V/Ni or V/(Ni+V) among oil fields of the same rock basin describes the trend of crude petroleum migration in the direction of decreasing order [2, 5]. From Table 2, the values of the V/Ni and V/(Ni+V) ratios for TB-2 are higher than that of TB-1 indicating that crude petroleum migration may occur from the oil field of TB-2 to that of TB-1 in the Tano Basin. The lesser the magnitude of V/Ni or V/(Ni+V), the higher the maturity level of the crude petroleum and vice versa [1, 4, 5, 15]. Therefore, SB-2 is the most matured crude petroleum, and TB-2 is the least. Based on V/Ni and V/(Ni+V) ratios as oil field maturity indicators, Saltpond oil field is the most matured followed by Jubilee, and the least is TEN oil field. This trend in the values of V/Ni and V/(Ni+V) ratios among the oil fields supported the postulate by others that Saltpond Basin is the oldest sedimentary rock in the province of Gulf of Guinea [33, 34].

From the results obtained, the trend in V/Ni and V/(Ni+V) ratios among the three oil fields is a reverse to the trend by Fe concentrations as discussed earlier. This difference in the trends disagreed with the idea proposed by Katchenkov (1952) that the concentration of Fe is higher in younger oil fields [4, 36]. From this study, it was evident that Saltpond oil field as the most matured [33, 34] among the three recorded the highest Fe concentration, whilst TEN, the least matured oil field, recorded the lowest.

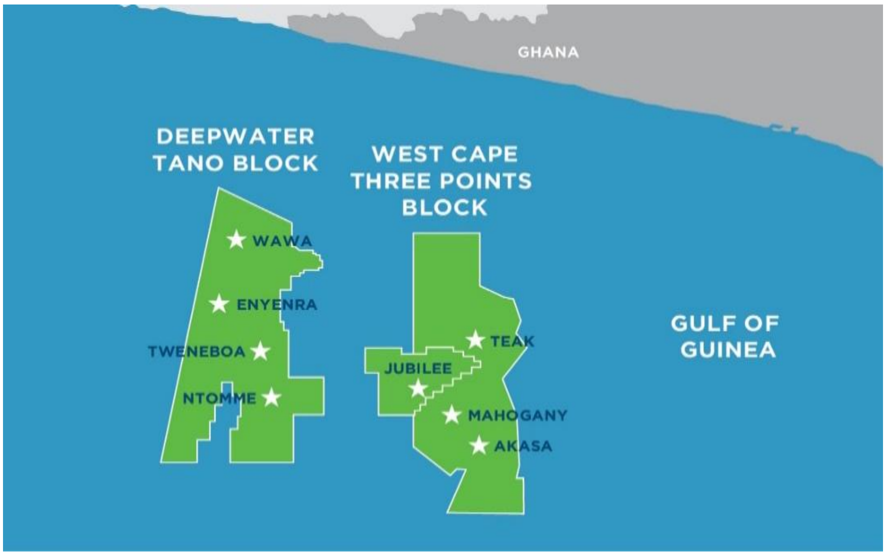

Fig. 3. Jubilee and TEN oil fields of Ghana [30]

Table 1. Elemental concentrations of the samples

	Elements		**Elemental concentration in ppm**			
			Tano Basin		**Saltpond Basin**	
	Name	Symbol	TB-1	TB-2	SB-4	SB-2
Nonmetals	Sulphur	S	2750	2810	1230	1880
	Bromine	Br	0.1330	0.0126	BDL	0.3960
	Chlorine	Cl	BDL	BDL	213.00	646.00
	Selenium	Se	BDL	BDL	BDL	0.0575
Semimetal	Germanium	Ge	0.6790	0.6810	1.6100	0.2620
Alkali metals	Potassium	K	27.100	22.700	49.600	25.800
	Rubidium	Rb	0.1570	0.0920	0.3400	0.0712
Alkaline Earth Metals	Calcium	Ca	2.6800	4.3300	54.200	265.00
	Barium	Ba	BDL	BDL	4.6300	3.7800
	Strontium	Sr	0.0288	0.0936	BDL	0.2270
Transition Metals	Scandium	Sc	1.3800	BDL	2.5300	3.9600
	Titanium	Ti	BDL	1.2200	BDL	BDL
	Vanadium	V	0.4230	1.7900	0.4780	BDL
	Chromium	Cr	18.600	18.700	15.400	17.300
	Manganese	Mn	BDL	BDL	BDL	3.3200
	Iron	Fe	34.300	32.800	87.300	79.700
	Cobalt	Co	1.1800	1.0400	3.1300	1.2100
	Nickel	Ni	10.000	8.6400	23.400	6.9400
	Copper	Cu	6.6200	2.0800	6.4600	1.7800
	Zinc	Zn	2.8500	0.3290	1.1800	0.2920
	Gold	Au	0.8170	0.1340	0.0387	0.8650
	Yttrium	Y	0.0641	0.1010	0.1550	0.0552
	Zirconium	Zr	0.1170	0.0888	0.2160	0.0845
	Niobium	Nb	0.1790	0.1470	0.2220	0.0884
	Molybdenum	Mo	0.1500	0.0590	0.1200	0.1000
	Tantalum	Ta	0.1730	0.0848	BDL	1.4000
	Iridium	Ir	3.1500	2.5600	5.8100	0.1730
Basic Metals	Indium	In	150.00	90.800	26.400	58.700
	Lead	Pb	BDL	BDL	BDL	0.2700
	Bismuth	Bi	BDL	BDL	BDL	0.0323

Table 2. Comparison of vanadium-nickel ratios to sulphur composition

Rock Basin	Sample	Concentration in ppm			V/Ni	V/(Ni+V)
		V	Ni	S		
Saltpond Basin	SB-2	0.0000	6.9400	1880	0.0000	0.0000
	SB-4	0.4780	23.4000	1230	0.0204	0.0200
	Average	0.2390	15.1700	1555	0.0158	0.0155
Tano Basin	TB-1	0.4230	10.0000	2750	0.0423	0.0406
	TB-2	1.7900	8.6400	2810	0.2072	0.1716
	Average	1.1065	9.3200	2780	0.1187	0.1061

Also, V/Ni and V/(Ni+V) ratios for the four crude samples TB-1, TB-2, SB-2 and SB-4 were extremely < 0.5 suggesting an emphasis on marine organic matter origination [4, 16]. There is a significant linear trend between V/Ni and V/(Ni+V) ratios concerning sulphur contents from Table 2. This research results agreed with other researchers that suggested that the lesser the value of V/Ni and V/(Ni+V) ratios for an oil field, the lesser the sulphur content [4, 9, 15, 16]. From this study, the sulphur content of Tano Basin is 1.7878 times greater than that of Saltpond Basin. Therefore, Saltpond Basin is more matured and produces much quality crude petroleum with less sulphur content than the Tano Basin.

Table 3 describes the concentrations of scandium and yttrium, rare earth metal elements, that were estimated by the study. The purpose was to predict the existing relationship between the calculated V/Ni ratios and concentrations of scandium and yttrium to characterise the oil fields and the rock basins.

In the Saltpond Basin, the concentration of Sc in SB-2 was higher than that of SB-4, but the reverse was observed for Y, although both were samples from the same oil field. TB-1 and TB-2 were both obtained from the Tano Basin but TB-1 was relatively richer in Sc and Y than TB-2. These disparities in elemental concentrations among the two oil wells from the same oil field also emphasizes non-uniform distribution of chemical elements in the Saltpond sedimentary rock. Concerning the three oil fields, the concentrations of Sc decreased from Saltpond, Jubilee and TEN in that order; whilst the order for Y was Saltpond, TEN and Jubilee. Therefore, Saltpond oil field recorded relatively higher concentration of the rare earth metal elements that were investigated. The higher concentration of Sc and Y in Saltpond Basin suggest that the sedimentary rock is geographically located relatively nearer to McCarthy Hills at Weija, Greater Accra, as compared to Tano Basin [37]. The hills have faults that generate seismic waves at relatively low amplitudes in Ghana, [37]. As a result of seismic disturbances, rare earth elements (Sc and Y) may travel from the upper mantle of the earth to the crust where sedimentary rock is located [17]. Therefore, the higher concentrations of the rare earth metal elements in the Saltpond oil field is possibly due to seismic waves effect from McCarthy Hills.

Figs. 4 and 5 are bivariate graphs of the two vanadium-nickel ratios (Predictor) as abscissa and scandium concentration (dependent) as ordinate. The magnitude of the slope of each bivariate graph represent inverse relation change between the two parameters.

From the equation shown in Fig. 4, it can be seen that the incremental change in scandium concentrations among the three oil fields is 13.918 times greater as compared to the decremental change in vanadium nickel ratios of the same oil fields and vice versa. Also, the bivariate graph for Fig. 5 produced an equation which described similar phenomenon. The linear correlation coefficients obtained from both graphs are 0.7855 and 0.8034 respectively, which implies strong correlation. Therefore, changes in scandium concentration can equally be used as a tool to characterise crude petroleum, oil fields and rock reservoirs just as the vanadium-nickel ratio [5, 18].

The experiment came up with scientifically human and environmental accepted toxic metals [11, 31]. These heavy metal elements are Cr, Pb, Mn and Bi. Concerning the three oil fields, Saltpond oil field on the average recorded greater number of toxic metals as compared to Jubilee and TEN oil fields. The greater number of heavy metals in crude petroleum recorded suggests that crude petroleum spillage and waste from Saltpond oil field may cause greater ecological imbalance to lives than that from Jubilee and TEN oil fields [1, 10, 12, 38]. However, for the four crude petroleum samples used for the study, metal elements in traces that are biologically toxic to the environment were relatively low in concentrations [1]. Therefore,

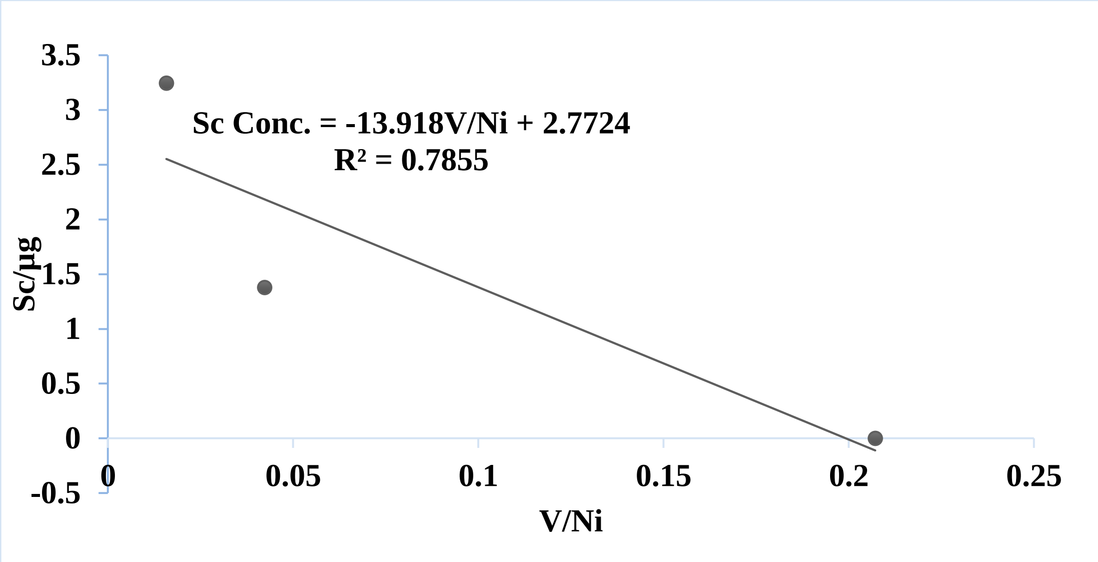

Fig. 4. Bivariate Graph of Scandium Concentration Versus V/Ni Ratio

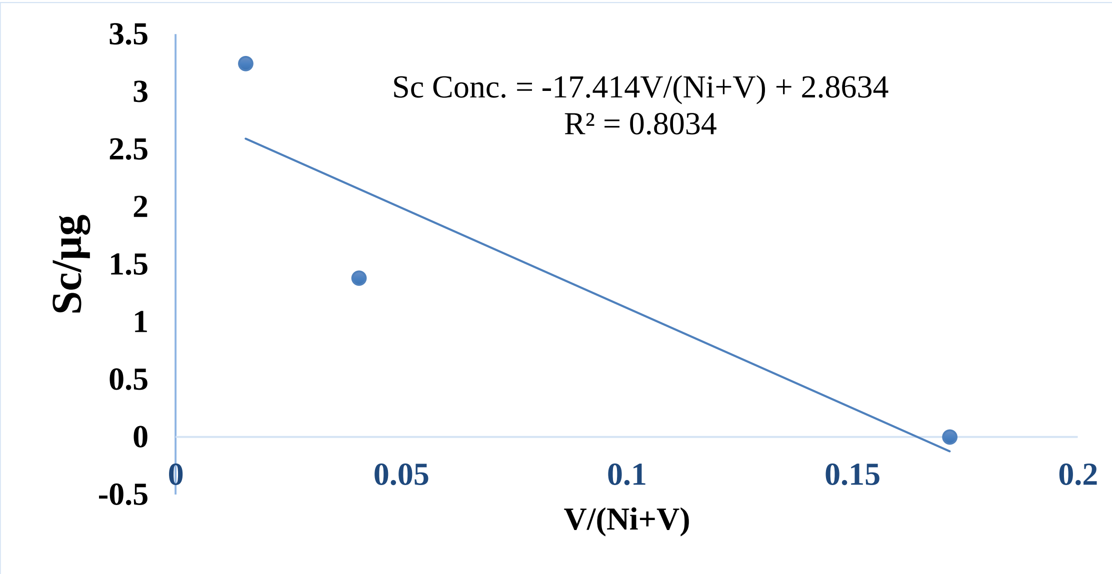

Fig. 5. Bivariate Graph of Scandium Concentration Versus V/Ni Ratio

Table 3. Scandium and yttrium concentrations versus vanadium-nickel ratios

Rock Basin	Sample	Concentration in ppm		V/Ni	V/(Ni+V)
		Sc	Y		
Saltpond Basin	SB-2	3.9600	0.0552	0.0000	0.0000
	SB-4	2.5300	0.1550	0.0204	0.0200
	Average	3.2450	0.1051	0.0158	0.0155
Tano Basin	TB-1	1.3800	0.0641	0.0423	0.0406
	TB-2	0.0000	0.1010	0.2072	0.1716
	Average	0.6900	0.0826	0.1187	0.1061

based on the ultra-trace level (< 100.0 part per million or < 0.01 weight per cent) of toxic metal concentration, crude petroleum samples from the three oil fields in Ghana studied can be considered to be of good quality [1].

4. CONCLUSIONS

In all, thirty elements were identified qualitatively from each sample and the concentration for each identified element quantified. The concentration levels of the twenty-six metal elements were ultra-trace (< 0.01 weight per cent) indicating quality crude petroleum of less refinery cost. Also, the concentration levels of heavy metal elements that may cause ecological imbalance to lives when exposed are in ultra-trace.

The value of vanadium-nickel ratio estimated for each crude petroleum sample was less than 0.5. Based on the values of vanadium-nickel ratios, Saltpond oil field is found to be the most matured followed by Jubilee and TEN. The oil fields maturity as deduced from the crude petroleum samples investigated correspond to the maturity of the respective sedimentary rock basins. The higher maturity of Saltpond Basin agrees with the postulate that Saltpond Basin is the oldest hydrocarbon source rock along the Gulf of Guinea. There is a significant difference in the values of vanadium-nickel ratios of TB-1 and TB-2 from the same sedimentary rock. This implies that the hydrocarbon migration in the Tano Basin occurs from the TEN oil field to Jubilee.

The research came up with healthy bivariate graphs of each of negative gradient between the scandium concentrations (dependent) and vanadium-nickel ratios (predictor) of the oil fields. Also, the magnitudes of the gradients from the bivariate graphs depicts an inverse significant change between the two parameters with strong correlation coefficient each. From the analyses of the bivariate quantities, it can be concluded that scandium concentrations among crude petroleum samples can be used as a tool for oil fields and sedimentary rock basins characterisations just as the vanadium-nickel ratios. Moreover, the effects of seismic activities from McCarthy Hills on Saltpond sedimentary basin suggested a relatively higher level of scandium and yttrium concentrations in SB-4 and SB-2 compared to TB-1 and TB-2 in the Tano Basin.

Concerning the origin of the crude samples, the presence of nickel and vanadium in the four samples in significant quantities suggests that Ghana's crude petroleum are of marine organic origin. However, the vast difference in Fe concentrations between Saltpond and Tano Basins indicates that the two sedimentary rock basins are geochemically different.

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COMPETING INTERESTS

Authors have declared that no competing interests exist but purposely for the advancement of knowledge. The crude petroleum samples used for this research are commonly used in our country. Also, the research was funded by personal efforts of the authors.

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