Trace Metals in Nigerian Crude Oils and Their Heavy-End Distillates

Abass A. OLAJIRE[†] and Rotimi A. ODERINDE*
Department of Chemistry, University of Ibadan, Ibadan, Nigeria
†Department of Pure and Applied Chemistry, Ladoke Akintola University of Technology, Ogbomoso, Nigeria

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Energy dispersive X-ray fluorescence spectroscopy was used to determine Fe, Hg, V, Cd, Pb, Mn, Ni, Zn, Cu, As, and Se in samples of crude petroleum and their heavy residual oils boiling above 387°C (729°F) from different oil producing companies in Nigeria. Vanadium, nickel, iron, and copper are the most abundant elements, and their concentrations ranged from 14 to 99 ppm; 5.0 to 11 ppm; 43 to 110 ppm and <0.05 to 54 ppm respectively. Other metals, i.e. Cadmiun and manganese were observed at the 2.4 to 8.9 ppm level while mercury, zinc, lead, arsenic, and selenium are present in very low level (0—1.4 ppm). An attempt was made to establish the distribution pattern of vanadium and nickel in the crude petroleum and their heavy residual oils.

Recently, there have been a number of studies on analysis of petroleum and petroleum products for trace elements.[1—7] This interest is because of their importance both in genesis of petroleum and its refining. The present trend in catalytic cracking is in the direction of utilizing heavier oil as feedstock, hence the concentrations of metal contaminants in the heavy-residual oil called for great attention. The elements such as As, Se, Pb, V, and Ni poison the catalyst used in the refineries and automobiles, with a resultant loss in catalyst activity and poor product yields. The refiner therefore must know especially the concentrations of nickel and vanadium in stocks being charged to fluid cracking units. Also, elements such as Cd, As, Se, Hg, and Pb can cause accumulative detriment to the environment when they are present in fossil fuels.

In the present study, we report the analysis of trace metals in crude oils and their heavy-end distillates by energy dispersive X-ray fluorescence spectroscopy (ED-XRF). The minimization of matrix effect was accomplished by digestions of the sample followed by concept of sample preconcentration prior to determination. A correlation analysis between the concentration of V : Ni ratio of crude petroleum and heavy residual oil was made in attempt to obtain information on the distribution pattern of these metal contaminants in the crude petroleum and heavy residual oil.

Experimental

Apparatus: Energy dispersive X-ray analysis were done with XR 300 50KV spectrometer (Link Analytical limited, Halifax Road, England) in conjuction with a Si(Li) detector and interfaced to an AN 10000 computer based multichannel analyzer (MCA) connected with the XR 300 spectrometer module. A rhodium anode 50-W side window X-ray tube was operated in a pulsed mode at an anode voltage of 40 kV and at an anode current of 800 μA, ensuring a dead time of ⩽50% through the whole system. A thin anode filter was used to reduce spectra background. All samples were irradiated for 200 s lifetime.

Thin-film samples were mounted between 0.25 ml Mylar films (Ultra thin Mylar, Sonar International, Inc., Tuckahoe NY 10707, U.S.A.) in a polypropylene sample holder (Type A 5340 spectro cups, Microscience Div.).

Oil Samples: Samples of crude petroleum supplied by Shell Petroleum Development Company, Mobil Oil Producing, and Gulf Oil Company were packed in sealed glass container (1 dm^3 capacity) and stored in the refrigerator at 4°C prior to laboratory analysis.

Chemicals: All the chemicals used for this analysis are as specified by the Committee on Analytical Reagents of American Chemical Society.

Sample Preparation: All glasswares were washed and rinsed with distilled water, and then soaked overnight in chromic acid cleaning solution. They were then thoroughly rinsed in deionized distilled water and dried by inverting on clean paper. The flasks were later dried at 110°C in an oven and were placed in dessicators to cool.

Preparation of Heavy-End Distillates: The distillates were prepared from six crude oils- Bonny light, Forcados, UPC, and Oloibiri (Shell Petroleum Development Company); Eket (Mobil Oil Producing), and Escravos (Gulf Oil Company); — by distillation of the crudes under controlled true boiling point distillation conditions as done in the refineries, using a Vigoureux type of distilling column having a length of 80 cm and diameter of 2.5 cm. The column was wrapped with a heating coils connected to a heating regulator. The distillation column was filled with "Helipack" at a reflux ratio of 15 : 1. The light and middle distillates were collected at 50°C intervals in the boiling range up to a maximum of 387°C. Distillation was carried out at atmospheric pressure up to a still liquid temperature of 300°C, beyond which reduced pressure of 40 mmHg (1 mmHg=133.322 Pa) was used. The heavy-end distillate left in the flask was cooled and kept in the refrigerator at 4°C prior to digestion.

Sulfuric-Nitric Acid Digestion: The samples were digested as described by Walker et al.[8] Five grams each of the crude petroleum and heavy residual oils were placed in 600 ml Erlenmeyer flask and 25 ml of sulfuric acid and 50 ml nitric acid were added. The flask was heated on a hot-plate under a hood until fumes of sulfuric acid begin to evolve. The flask was slightly cooled and 25 ml nitric acid was added dropwise and the solution was heated again to white fumes. Subsequently, 20 ml of 70% perchloric acid was added. Evaporated acid (HNO_3) was replaced by adding 25 ml aliquots until the digestate was clear and colorless. The solution was evaporated until the volume had been reduced

Table 1. Trace Metals in Nigerian Crude Oils and Their Heavy-End Distillates

	Metals [a)] ppm										
Oil samples	Cu	Fe	Hg	V	As × 10^{-3}	Zn × 10^{-1}	Ni	Pb	Cd	Se × 10^{-2}	Mn
Forcados	38±3	55±3	N.D.	54±2	<0.20	<0.10	11±1	0.5±0.1	7.2±0.4	<0.10	2.8±0.6
Oloibiri	21±1	81±4	N.D.	29±1	<0.20	<0.10	6.2±0.3	<0.01	6.7±0.4	<0.10	6.2±0.5
Bonny light	22±1	78±4	N.D.	14±1	<0.20	<0.10	5±0.3	0.4±0.04	6.1±0.5	<0.10	2.8±0.3
UPC	22±1	87±5	<0.02	57±4	<0.20	<0.10	11±0.3	0.5±0.03	5.7±0.3	<0.10	4.2±0.3
EKET	54±3	59±3	<0.02	64±4	<0.20	<0.10	7±0.4	1.4±0.1	8.9±0.5	<0.10	4.1±0.4
Escravos	32±2	110±10	<0.02	99±6	<0.20	<0.10	8±0.4	0.63±0.1	5.8±0.5	<0.10	3.7±0.3
Forcados heavy	30±2	86±6	N.D.	54±4	<0.20	<0.10	9.1±0.4	0.7±0.04	7.4±0.4	<0.10	2.8±0.5
Cloibiri heavy	<0.05	43±2	N.D.	34±3	<0.20	<0.10	5.9±0.3	<0.01	5.8±0.6	<0.10	2.7±0.3
Bonny heavy	18±2	89±5	N.D.	14±1	<0.20	<0.10	5.5±0.4	1.12±0.2	5.3±0.4	<0.10	2.4±0.2
UPC heavy	19±1	88±6	<0.02	64±4	<0.20	<0.10	11±1	<0.01	5.9±0.4	<0.10	2.5±0.2
EKET heavy	43±3	46±3	N.D.	29±2	<0.20	<0.10	6.5±1	1.1±0.1	8.9±0.6	<0.10	3.8±0.2
Escravos heavy	27±3	66±4	<0.02	99±6	<0.20	<0.10	7.5±0.4	0.9±0.1	5.4±0.3	<0.10	2.8±0.2

a) Values are means of triplicate determinations; ± Standard deviation of the means. N.D. =not detected.

to 10 ml. The remaining mixture was transferred to 100 ml volumetric flask and diluted to mark with deionized distilled water.

A reagent blank was prepared by using 25 ml sulfuric acid and 50 ml nitric acid and 20 ml of 70% perchloric acid in a 600 ml Erlenmeyer flask and the entire sequence of steps was followed as described for the oil samples preparation.

ED-XRF Analysis: The digestates were preconcentrated as described by Ellis et al.[9)] Twenty-five ml aliquots of the samples and the reagent blank were made up to 100 ml with deionized distilled water. The pH's of the solutions were adjusted to 4.00±0.05 and bufferred with 2 ml of 0.1 M (1 M=1 mol dm^{-3}) potassium hydrogen phthalate solution (pH 4). Two ml of 1% (w/v) methanolic solution of sodium dibenzylcarbamodithioate (NaDBDTC) was added. The solution was stirred intermittently for 15 min. The precipitate formed was aged for a further 15 min. The solution was then filtered under vacuum through a 25 mm (0.45 μm pore) membrane filter. The precipitate was washed with deionized distilled water. The filter was air-dried and mounted between 0.25 ml Mylar film on a standard 31.5 mm diameter specimen cup. The concentration of the metals was determined as follows:

$$\text{ppm of the metal in the sample material} = \frac{\text{microgram } (\mu\text{g}) \text{ of the metal in the precipitate} \times 4}{\text{grams of sample.}} \quad (1)$$

Calibration Curves: Multiple elements calibrations were established over the range of 0—100 μg. A mixed standard solution was prepared to contain different concentration of each element. Into 100 ml standard flasks labelled A, B, C, and D were added 0.50, 1.00, 2.00, and 5.00 ml of standard solutions of each element respectively and made up to mark with deionized distilled water. The preparation was done in duplicate. The metals were precipitated out with sodium dibenzylcarbamodithioate as done for the samples and analyzed by ED-XRF spectroscopy. From these data, the calibration slope, linearity and linear range were established.

Results and Discussion

The results of the analysis were presented in Table 1 with standard deviation values based on the triplicate analysis of the samples. It is clear from the result that there was slight decrease in the concentrations of some of the metals in the residual oils as compared with the crude petroleum. The decrement could be explained as either due to volatilization of the metals or trapping of the metals into the light and/or middle distillates during distillation. Among the metals which act as catalyst poison, the concentrations of vanadium and nickel are quite appreciable, ranging from 14 to 99 ppm and 5 to 11 ppm respectively. Other metals, i.e. copper, cadmium, and manganese were observed at <0.05 to 54 ppm level while mercury, zinc, arsenic, lead,and sele-

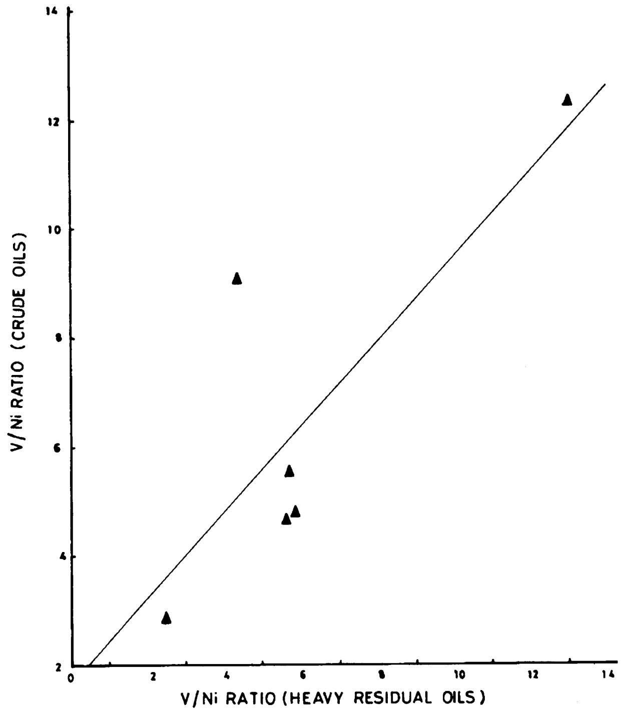

Fig. 1. Linear Relationship of V/Ni ratio of crude oils and heavy residual oils known as No. 6 oils.

nium were present in very low level (0—1.4 ppm). The relatively high iron (43 to 110 ppm) level is noteworthy. This could suggest the robustness of heam source compared with chlorophyll source for the petroleum.

The distribution pattern of these metal contaminants, i.e. vanadium and nickel in the crude and heavy residual oils was established by making a plot of the V/Ni ratio of the crude petroleum against that of the residual oils (Fig. 1). The points scattered around the common line expressed by the equation, $Y = 0.78X + 1.66$, where Y and X represent the V/Ni ratio of crude petroleum and heavy residual oils respectively. The equation predicts that the V/Ni ratio of the residue to be about three-quarter of that of crude petroleum.

However, these results show unequivocally that vanadium and nickel present in crude petroleum are concentrated in the residue. The utilization of this residue as feedstock will therefore poses a lot of industrial problems, as these elements including sulfur poison the catalyst used in the refinery, resulting in poor product yield and cause corrosion of processing units. The refiner should therefore find a means of keeping such contaminants under control.

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