

# Physical Sciences Section

Pak. j. sci. ind. res., vol. 37, no. 9, September 1994

## TRACE METAL ANALYSIS IN FRESH AND WEATHERED CRUDE OILS

A. A. OLAJIRE\* AND R. A. ODERINDE

Department of Chemistry, University of Ibadan, Ibadan, Nigeria

(Received July 21, 1992; revised April 2, 1994)

Energy dispersive X-ray fluorescence spectroscopy was used to determine Fe, Cd, Pb, Ni, Mn, Zn, Cu, V, As, Hg and Se in the Nigerian fresh and weathered crude oils. Weathered crudes consisted of fresh crudes weathered for 2, 7 and 14 days under ambient outdoor conditions. Vanadium, nickel, iron and copper concentrations in both the fresh and weathered crudes ranged from 12 to 114 ppm; 4.2 to 12 ppm; 45 to 182 ppm and 22 to 81 ppm respectively. Other metals, i.e. lead, cadmium and manganese were observed at the 0.42 to 11 ppm level whereas mercury, zinc, arsenic and selenium were present in very low level (0 - 0.02 ppm). For the weathered report, the values were increasing as weathering progressed. An attempt was made to assess the applicability of V:Ni ratio for passive tagging of oils.

**Key words:** Fresh and weathered crudes, Trace elements; ED - XRF techniques.

### Introduction

Petroleum spillage occurring as a result of natural seepage of crude petroleum from deposits, accidental rupture of off-shore oil wells and oil pipelines leakage are of concern in the marine environment. Now-a-days, most environmental protection agencies are adopting the policy of 'polluter pay principle'; polluters may want to ascertain their responsibility. This requires accurate identification of spilled oils.

Various techniques have been suggested for identifying the source of crude oils spills; amongst these is trace elemental analysis [1-4]. In the present study, energy dispersive X-ray fluorescence spectroscopy (ED-XRF) technique was used for multi-elemental analysis of petroleum and its weathered products and the applicability of the V:Ni ratio for passive tagging of oil was assessed. The minimization of matrix effect was accomplished by digestion of the sample followed by sample preconcentration prior to determination.

### Materials and Methods

**Instrumentation.** Energy dispersive X-ray analysis were done with XR 300 50KV spectrometer (Link Analytical Limited, Halifax Road, England) in conjunction with a Si(Li) detector and interfaced to an AN 10,000 computer based multichannel analyser (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 40KV and at an anode current of 800 $\mu$ A, ensuring a dead time of 50% through the whole system. A thin anode filter was used to reduce spectral background. All samples were irradiated for 200s lifetime. Thin-film samples were mounted between 0.25ml Mylar films (Ultra thin Mylar, Sonar International, Inc., Tuckahoe NY 10707, USA) in a polypropylene

sample holder (Type A 5340 spectro cups Microscience Div.).

**Oil samples.** Samples of crude petroleum, supplied by Shell Petroleum Development Company and Chevron Nigeria Limited, were packed in sealed glass containers (1 dm<sup>3</sup> capacity) and stored in the refrigerator at 4° prior to laboratory analysis.

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

**Weathering procedure.** The fresh crude oils were weathered as described by Riley *et al.* [5]. The oil samples were weathered by spilling one pint of the oil in rectangular fiber glass containers, 40 x 32 x 4cm in dimension. Seawater, drawn from Bar Beach at Lagos, was constantly circulated through the containers. The weathering was performed under ambient outdoor conditions (Temperature, 32  $\pm$  4°; Wind, moderate) during the dry season, and for periods of 2, 7 and 14 days each. The residual water and particulate matter were separated from the oil by spinning the sample in a centrifuge at 6,000 rpm for 20 mins; excess water was removed by siphoning.

**Sulfuric-nitric acid digestion.** The samples were digested as described by Walker *et al.* [6]. Five grams each of the fresh and weathered oils was 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 sulfuric acid began to fume. The flask was slightly cooled and 25 ml nitric acid was added dropwise and the solution was heated again until white fumes evolved. Subsequently, 20 ml of 70% perchloric acid\* was added (Caution: Perchloric acid should be added before nitric acid evaporates to fuming). Evaporated acid, HNO<sub>3</sub> was replaced by adding 25 ml aliquots until the digestate was clear and colourless. The solution was evaporated until the volume had been reduced to 10 ml. The remaining

\* Department of Pure and Applied Chemistry, Ladoké Akintola University of Technology, Ogbomoshó, Nigeria.

mixture was transferred to a 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.* [7]. Twenty-five ml aliquots of the samples and the reagent blank were made up to 100 ml with deionized distilled water. The pH of the solutions were adjusted to  $4.00 \pm 0.05$  and buffered with 2 ml of 0.1M ( $1M = 1 \text{ mol dm}^{-3}$ ) potassium hydrogen phthalate solution (pH 4). Two ml of 1% (W/V) methanolic solution of sodium dibenzyl dithiocarbamate (NaDBDTC) was added. The solution was stirred intermittently for 15 mins. The solution was then filtered under vacuum through a 25 mm ( $0.45\mu\text{m}$  pore) membrane filter. The precipitate was washed with deionized distilled water. The filter was air dried and mounted between 0.25ml Mylar film on a standard 31.5mm diameter specimen cup. The metal concentrations were determined by reading of the calibration curves.

### Results and Discussion

Results of the trace metal analysis of the Nigerian fresh and weathered oils are presented in Table 1. For each of the fresh and weathered oils investigated, the most abundant trace metals observed were iron, vanadium, copper and nickel; and their concentrations ranged from 45 to 182ppm; 12 to 114ppm; 22 to 81 ppm and 4.2 to 12 ppm respectively. The relatively high iron (45 to 182ppm) level is noteworthy. This could suggest the robustness of heam source compared with chloro-

phyll source for the petroleum. Other metals, i.e. lead, cadmium and manganese were observed at the 0.42 to 11 ppm level while mercury, zinc, arsenic and selenium were present in very low level (0 - 0.02 ppm). It is clear from the results of the analysis that the concentration of the metals increases as weathering progress. This could be caused by loss of volatile materials which do not contain metals, thereby leading to concentrations of the metals in the weathered products.

Among the trace metal indices, the ratio of vanadium to nickel concentration was the most widely applied parameter in the studies of petroleum trace metals. The V:Ni ratio was calculated for each sample of both fresh and weathered products, and the results are reported in Table 2. Other trace metal indices were also calculated. Statistical analysis using Duncan's multiple range test (DMRT) was carried out to test the significance of differences among the trace metal indices at the prescribed level of significance as weathering progressed (Table 3). The result indicates that V/Ni, V/Mn, V/Fe and V/Cd ratios were independent of weathering at 1% level of significance ( $P \leq 0.01$ ). The slight variations between the values of these ratios of fresh and weathered crude oils are presumed to be due to experimental errors in analysis.

The result does not prove, however, that the nitrogen complexes (porphyrins) or other organometallic compounds containing nickel, vanadium and iron are not susceptible to environmental degradation, but appears to confirm that the ratio can be used to fingerprint the source of oil spill and to establish whether two samples of oil originate from the same source. As part of our continuing interest in this subject, work is still in progress on whether these organometallic compounds are affected by weathering.

TABLE 1. TRACE METALS IN NIGERIAN FRESH AND WEATHERED CRUDE OILS ANALYSED.

Metals <sup>#</sup> ppm	Fresh crude			2-Day unweathered sample			7-Day weathered samples			14-Day weathered samples		
	BL	FC	ES	BL	FC	ES	BL	FC	ES	BL	FC	ES
Cu	22±1	38±3	32±2	41±4	42±4	66±6	41±4	81±7	59±5	39±4	74±7	56±6
Fe	78±4	55±3	110±10	100±9	51±5	137±12	115±9	54±5	182±16	92±5	45±4	157±9
V	14±1	54±2	99±5	12±0.6	59±3	114±6	13±1	69±4	109±6	14±1	64±3	104±6
Cd	6.1±0.5	7.2±0.4	5.8±0.5	4.7±0.2	11±1	8.5±0.5	4.8±0.3	9.3±1	8.8±1	n.d	8.7±1	11±0.1
Zn	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Hg	n.d	n.d	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Ni	5.0±0.3	11±1	8.0±0.4	4.3±0.2	11±1	9.4±0.5	4.2±0.5	4.2±0.2	12±1	9.0±0.4	4.3±0.2	8.8±0.5
As x 10 <sup>-3</sup>	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Pb	0.4±0.04	0.5±0.1	0.6±0.1	1.7±0.1	1.8±0.1	0.8±0.04	1.6±0.1	2.1±0.1	2.7±0.2	1.4±0.1	n.d	2.1±0.1
Se	<0.001	<0.001	<0.001	n.d	n.d	<0.001	<0.001	n.d	<0.001	<0.001	<0.001	<0.001
Mn	2.8±0.3	2.8±0.6	3.7±0.3	3.3±0.3	4.0±0.4	3.7±0.4	2.8±0.1	4.0±0.4	3.4±0.2	3.0±0.3	3.3±0.2	4.2±0.3

BL = Bonny light crude. FC = Forcados crude. ES = Escravos crude. n.d = not detected. # = Values are means of triplicate determinations. ± Standard deviation of the means.

TABLE 2. TRACE METAL INDICES OF THE CRUDE OILS ANALYSED.

Metal indices	Fresh crude			2-Day unweathered samples			7-Day weathered samples			14-Day weathered samples		
	BL	FC	ES	BL	FC	ES	BL	FC	ES	BL	FC	ES
V/Ni	2.80	4.91	12.4	2.80	5.4	12.1	3.10	5.80	12.1	3.30	5.30	11.8
V/Cu	0.64	1.42	3.10	0.29	1.40	1.70	0.32	0.85	1.80	0.36	0.86	1.90
V/Pb	35	108	165	7.06	32.8	142	8.1	32.8	40.4	10	ND	49.5
V/Fe	0.18	0.98	0.90	0.12	0.20	0.83	0.11	0.30	1.60	0.15	1.40	0.66
V/Mn	5.0	19.3	26.8	3.6	14.8	30.8	4.6	17.2	32.0	4.7	19.4	24.8
V/Cd	2.3	7.5	17.1	2.6	5.4	13.4	2.7	7.4	12.4	ND	7.4	9.4

ND = Not determined.

TABLE 3. VARIATION BETWEEN THE METAL INDICES\* OF FRESH AND WEATHERED OIL SAMPLES USING DUNCAN'S MULTIPLE RANGE TEST AT 1% LEVEL OF SIGNIFICANCE ( $P \leq 0.01$ ).

Weathering period	V/Ni			V/Cu			V/Fe			V/Cd			V/Pb			V/Mn		
	BL	FC	ES	BL	FC	ES	BL	FC	ES	BL	FC	ES	BL	FC	ES	BL	FC	ES
Fresh samples	2.80 <sup>a</sup>	4.91 <sup>c</sup>	12.4 <sup>a</sup>	0.64 <sup>a</sup>	1.42 <sup>a</sup>	3.10 <sup>a</sup>	0.18 <sup>b</sup>	0.98 <sup>a</sup>	0.90 <sup>a</sup>	2.30 <sup>b</sup>	7.50 <sup>a</sup>	17.1 <sup>a</sup>	35 <sup>a</sup>	108 <sup>a</sup>	165 <sup>a</sup>	5.0 <sup>a</sup>	19.3 <sup>a</sup>	26.8 <sup>a</sup>
2-Day weathered samples	2.80 <sup>a,b</sup>	5.4 <sup>a,b</sup>	12.1 <sup>a</sup>	0.29 <sup>b</sup>	1.40 <sup>b</sup>	1.70 <sup>b</sup>	0.12 <sup>a,b</sup>	1.20 <sup>a,b</sup>	0.83 <sup>a,b</sup>	2.60 <sup>a,b</sup>	5.40 <sup>b</sup>	13.40 <sup>b</sup>	7.06 <sup>b</sup>	32.8 <sup>b</sup>	142 <sup>a</sup>	3.6 <sup>a</sup>	14.8 <sup>a</sup>	30.8 <sup>a</sup>
7-Day weathered samples	3.10 <sup>a,b</sup>	5.80 <sup>a</sup>	12.1 <sup>a</sup>	0.32 <sup>b</sup>	0.85 <sup>b</sup>	1.80 <sup>b</sup>	0.11 <sup>b</sup>	1.30 <sup>a,b</sup>	0.60 <sup>b</sup>	2.70 <sup>a</sup>	7.40 <sup>b</sup>	12.40 <sup>b</sup>	8.1 <sup>b</sup>	32.8 <sup>b</sup>	40.4 <sup>b</sup>	4.6 <sup>a</sup>	17.2 <sup>a</sup>	32.0 <sup>a</sup>
14-Day weathered samples	3.30 <sup>a</sup>	5.30 <sup>b,c</sup>	11.8 <sup>a</sup>	0.36 <sup>b</sup>	0.86 <sup>b</sup>	1.90 <sup>b</sup>	0.15 <sup>a,b</sup>	1.40 <sup>a</sup>	0.66 <sup>a,b</sup>	**	7.40 <sup>a</sup>	9.40 <sup>c</sup>	10 <sup>b</sup>	**	49.5 <sup>b</sup>	4.7 <sup>a</sup>	19.4 <sup>a</sup>	24.8 <sup>a</sup>

\* Means followed by the same alphabets in the superscript and occupying the same column are not significantly different using DMRT at 1% level of significance ( $P \leq 0.01$ ). \*\* Not statistically analysed.

### Conclusion

The results shed some light on the effects of weathering of crude oil under simulated outdoor conditions. The main conclusion of the work is that the ratio of concentration of vanadium to nickel, iron, cadmium and manganese respectively in an oil sample appears to be unaffected by weathering to any significant extent allowing their use in fingerprinting the source of an oil spill.

**Acknowledgement.** The authors wish to thank Professor O.A. Afolabi of Federal Environmental Protection Agency; and Messrs Nkono, A. Nkono; Femi Ogunsola and Jonathan Adejumo; all of Obafemi Awolowo University for their technical assistance.

### References

1. A. F. Mohammad, B. Ahmed and S. Mohammad, *Ind. Eng. Chem. Prod. Res. Dev.*, **22**(4), 691 (1983).
2. T. R. Marija, *J. Serb. Chem. Soc.*, **52** (9), 499 (1987).
3. H. M. Al-Swaidan, A. Al-Gadi and A. A. Mohammed, *Orient. J. Chem.*, **4**(3), 221 (1988).
4. S. N. Sharma, *J. Sci. Ind. Res.*, **42**(6), 341 (1983).
5. R. G. Riley, B. L. Thomas, J. W. Anderson and R. M. Beam, *Mav. Environ. Res.*, **4**(2), 109 (1980).
6. H. H. Walker, J. H. Runnels and R. Merryfield, *Anal. Chem.*, **48**(14), 2056 (1976).
7. A. T. Ellis, D. E. Leyden, W. Wegscheider, B. B. Jablonski and W. B. Bodnar, *Anal. Chim. Acta*, **142**, 73 (1982).