International Journal of Advances in Engineering and Management (IJAEM)
Volume 3, Issue 11 Nov 2021, pp: 106-110 www.ijaem.net ISSN: 2395-5252

Determination of Vanadium Concentrations in Nigerian Crude Oils and Tar (Oil) Sands Using Instrumental Neutron Activation Analysis (Inaa)

[1]agaja S. A.And[2]ayourim P.
[1]*Industrial Safety and Environmental Technology*
[2]*Science Laboratory Technology Department*
Petroleum Training Institute
Effurun Delta State, Nigeria

Submitted: 25-10-2021 Revised: 31-10-2021 Accepted: 05-11-2021

ABSTRACT
Instrumental neutron activation analysis based on thermal neutrons from the Ghana Research Reactor – 1 facility was used to determine the Vanadium concentrations in Crude oil samples from Niger Delta basin and tar (oil) sands from Okitipupa in Ondo State. The concentration of Vanadium varied in the different samples in the crude oils ranged from $(0.2 - 2.7)\ \mu g g^{-1}$ and in the oil sands it was $189.42 \pm 28.41 \mu g g^{-1}$. Although, Nigerian crude oils showed low vanadium concentrations when compared with other crude oils elsewhere in the world. The vanadium concentration in the tar (oil) sands was significantly very much higher than the crude oils. This is due to their different geological formations and origin.
Keywords: Crude oils, Vanadium, Tar (oil) sands, Nigeria, INAA

I. INTRODUCTION

Knowledge of trace elements in crude oil is vital for exploration, production and during refining processes (Elirich, 1985). Trace elements in crude oils is directly correlates with light, medium and heavy crude oils (Barbooti, 2010). Vanadium is undesirable elements found in crude oil and its products also has undesirable effects in the refining process, causes corrosion in oil fired power plants and affects the catalyst activity (Qasim and Sardasht, 2018).

The nature of vanadium compounds in crude oil was first reported by Treibs (1934) who observed that part of the vanadium in Bitumen, shale asphat, and crude oil was in form of porphyrin complexes.

Vanadium is present in petroleum and bitumen in the form of metalloporphyrin chelate, or mixed tetradentate complex of transition metals (Todorovic, 1987). The assessment of vanadium content of bitumen is very important from exploration, refining and eco-toxicological perspectives. Vanadium traces in refining process are capable of causing corrosion of columns or poison catalysts used during refining (Oluwole et al, 1993).

Further studies (Mark et al, 2018; Bruce, 1978; Earl, 1969 and Milson et al, 1966) has added to the knowledge of vanadium in petroleum. Petroleum refiners have catalytically cracked progressively higher boiling distillate streams, catalyst losses due to vanadium have become more severe (Annie et al, 2015; Robert L., 1959; Gransch J., 1970).

The aim of this work is to determine vanadium concentration in crude oil samples from seven oil wells across the Niger Delta basin and tar (oil) sands from Okitipupa in Ondo State and compare their values with reported values elsewhere around the world.

II. MATERIALS AND METHODS

2.1 Samples Collection Sites

Crude oil samples were collected from onshore well heads within the Niger Delta basin lat. 5.233732 and long 6.25091 in Nigeria. The map, stratigraphy and sedimentology of Niger Delta basin was reported by Reijers (2011). The oil sands

International Journal of Advances in Engineering and Management (IJAEM)
Volume 3, Issue 11 Nov 2021, pp: 106-110 www.ijaem.net ISSN: 2395-5252

samples were collected from a deposit site in Okitipupa, Ondo State.

2.2 Sample Preparation

The samples were collected in clean plastic bottles (1 litre bottle). Samples were prepared by weighing 200mg on polyethylene films. They were then wrapped with the samples identifies on them. Samples were then parked into polyethylene capsule of diameter 1.60cm (rabbit capsule) and heat sealed. Standards reference material orchard leaves 1571 from the National Institute of Standard and Technology (NIST) were equally weighed as test samples.

2.3 Sample Irradiation and Counting

Samples and controls were irradiated in the Ghana Research Reactor (GHARR-1) at the Ghana Atomic Energy Commission, operating at 15kW at a thermal flux of 5 x 10^{11} n.cm^{-2}.s^{-1}. Samples were transferred into irradiation sites via pneumatic transfer system at a pressure of 0.60Mpa. The irradiation was categorized according to the half-life of the element of interest as shown in the irradiation scheme in table 1.

Table 1: Irradiation Schemes

Short Lived Radionuclides

Element	Target Isotope	Reaction	Product Nuclide	Half-Life (t ½)	Gamma ray Energies (KeV)	Irradiation Time (s)	Counting Time (s)
Al	^{27}Al	^{27}Al (n, ɣ)	^{28}Al	2.24min	1778.9		
Ca	^{48}Ca	^{48}Ca (n, ɣ)	^{49}Ca	8.7min	3084.4		
Cl	^{37}Cl	^{37}Cl (n, ɣ)	^{38}Cl	37.3min	1642.4, 2167.5	120	600
Mg	^{26}Mg	^{26}Mg (n, ɣ)	^{27}Mg	9.46min	843.8, 1014.4		
Mn	^{55}Mn	^{55}Mn (n, ɣ)	^{56}Mn	2.58min	846.7, 1810.7, 2112		
V	^{51}V	^{51}V (n, ɣ)	^{52}V	3.76min	1431.1		

After the irradiation radioactivity measurement of induced radionuclide was performed by a PC-based gamma-ray spectrometry set-up. It consists of an n-type HPGe detector coupled to a computer based multi-channel analyzer (MCA) via electronic modules. The relative efficiency of detector is 25% and its energy resolution of 1.8keV at gamma-ray energy of 1332 keV of ^{60}Co. Through appropriate choice of cooling-time, detector's dead time was controlled to be less than 10% identification of gamma-ray product radionuclide was identified through the energies and quantitative analysis of the concentration was by converting the counts as area under the photo peak by the comparator method (Landsberger, 1991). Both analyses were done using the gamma-ray spectrum analysis software, ORTC MEASTRO-32. For windows model A65-B32 version 6.05 UMCBI kernel version 6.06 connections-32 version 6.06.Validation of the technique for the experimental set up was done by irradiating a standard reference material (Orchard leaves 1571) for the period of time as the sample in the same location within the reactor. The analysis of the standard reference material in table 2 shows good agreement of measured values with the certified ones. The standard specifications for Bonny light crude oil was shown in table 3.

2.4 Determination of Elements Concentration in the Samples

The calculation of trace elements concentrations in the samples was carried out by the comparator method using the same geometry, equal weights of both sample and standard with the same irradiation, decay and counting times, the concentration of the elements in the samples was determined by the expression below (Ehmann and Diane, 1991).

$$C_{sample} = C_{std}\left[\frac{A_{sample}}{A_{std}}\right]$$

Where:

C_{sample} = Unknown concentration of the element in the sample

C_{std} = Known concentration of the element in the standard

A_{sample} = Activity of the sample

A_{std} = Activity of the standard

International Journal of Advances in Engineering and Management (IJAEM)
Volume 3, Issue 11 Nov 2021, pp: 106-110 www.ijaem.net ISSN: 2395-5252

Table 2: Irradiation of Standard Reference Material 1571 Orchard Leaves used for Validation

Element	No. of Radiation	Reported Values $mgkg^{-1}$	This work $mgkg^{-1}$
Al	3	Not Reported	12
Br	3	10	12
Ca	3	2.09	2.11
Cl	3	700	698
K	3	1.447wt%	1.40wt%
Mg	3	0.62wt%	0.64wt%
Mn	3	91	91
Na	3	82	81
V	3	Not Reported	37

Table 3: Specification for Nigerian Bonny Light Crude Oil

S/N		
1.	Specific gravity @ $60^{o}/60^{o}F$	0.8387 – 0.8498
2.	API @ $15.55^{o}C$	35.0 – 37.0 max
3.	Density @ $15.55^{o}C$	0.85 g/ml max
4.	Pour Point	$< 40^{o}F/4.44^{o}C$
5.	Sulphur content % Wt	0.14 max
6.	Color	Dark brown
7.	Kinematic viscocity @ $40^{o}C$	3.5 cst
8.	Acid number	0.39 max
9.	Reid Vapour Pressure (RVP)	6.52psi max
10.	Water and sediment	11% max
11.	Iron wt, ppm	1.00 max
12.	Nickel wt, ppm	4.00 max
13.	Vanadium wt, ppm	2.00 max

Source: Petroleum Analysis Laboratory PTI

III. RESULTS AND DISCUSSIONS

Table 4: Vanadium Concentrations (μgg^{-1}) in Crude Oil Samples from Niger Delta Basin

Sample (ID)	Vanadium in Crude Oils	Vanadium in Tar (Oil) Sand
W1	2.7 ± 0.4	189.40 ± 28.41
W2	0.20 ± 0.03	
W3	1.3 ± 0.2	
W4	1.5 ± 0.2	
W5	2.2 ± 0.3	
W6	0.8 ± 0.1	
W7	1.1 ± 0.2	

Data Behind are $\pm$ Standard Deviations

Table 5: Comparison of Concentration of Vanadium in Crude Oils Reported in this work with other Workers around the Globe

Element	USA[a]	Libya[a]	Venezuela[a]	Canada[a]	Middle East[b]	China[c]	Ghana[d]	Iraq[e]	Present work Nigeria
V	7.5	8.2	11.10	13.6	100	10.4	0.40	223.75	0.2 – 2.7

International Journal of Advances in Engineering and Management (IJAEM)
Volume 3, Issue 11 Nov 2021, pp: 106-110 www.ijaem.net ISSN: 2395-5252

a Filby and Shan, 1975; Hitchon et al, 1975
b Williams and Cawcey, 1963
c Chifiany et al, 1991
d Kpeblo et al, 2015
e Qasim and Sardash, 2018

Table 6: Comparison of Vanadium Concentrations in Nigeria Crude Oils Reported by this Work and other Workers

Element	Concentration	Unit	Author
Vanadium	11.2 – 29.2	μgg^{-1}	Akinlua et al, 2007
	0.009 – 1.832	μgg^{-1}	Nwachukwu et al, 1995
	3.70 – 40.0	μgg^{-1}	Udo et al, 1992
	0.54 – 1.195	μgg^{-1}	Oluwole et al, 1993
	0.642 – 0.10	μgg^{-1}	Ndiokwere, 1983
	22.5 – 1060	ngg^{-1}	Muhammad et al, 2013
	14000 – 99000	ngg^{-1}	Olajire and Oderinde, 1995
	1.95 – 7.94	μgg^{-1}	Kpeglo et al, 2015
	0.65 – 1.30	μgg^{-1}	Asoquo et al, 1995
	0.2 – 2.7	μgg^{-1}	Present study.

Table 7: Comparison of Vanadium Concentration in Nigeria Tar (oil) Sands

Element	Concentration	Unit	Author
Vanadium	1.69 – 69.44	μgg^{-1}	Asuquo et al, 1995
	0.31 – 0.44	μgg^{-1}	Oguntimehim and Ipinmoroti, 2007
	2.3 – 58.5	μgg^{-1}	Akinmosun and Gbolahan, 2010
	142.6 ± 0.02	μgg^{-1}	Ogunsuyi et al, 2012
	189.42 ± 28.41	μgg^{-1}	Present work.

Instrumental Neutron Activation Analysis (INAA) technique was used to analyze for vanadium in crude oil samples from Niger Delta basin and tar (oil) sands from Okitipupa in Ondo State using short-lived irradiation scheme. The crude oil result is shown in table 4. From the results it can be observed that the vanadium concentration in the crude oils varied appreciably between (0.2 – 2.71) μgg^{-1} in the samples. This is due to variation in geological and geographical locations of the oil fields. The nature of these elements and their relative abundance in crude oils can provide vital information about the origin, migration and maturation of petroleum as well as indicating the regional geochemical prospecting base (Chifang et al, 1991; Oluwole et al, 1993). Vanadium in petroleum could be used to explain the origin of petroleum from the decomposition of marine living organisms (Appentenget et al, 2012). Also, their ability to form complex or chelate on aγ and π bonding form with some organic compounds (Herberhold, 1972).

In table 6, comparing the value of vanadium concentrations observed in this work with other workers elsewhere around the globe, the vanadium concentrations in Nigerian crude oils were very low. Pointing to the fact that Nigerian crude oils were light crude oils. The vanadium concentration in tar sands from Okitipupa was higher than the values published by (Ogunsuyi etal, 2012, Oguntimehin and Ipinmoroti, 2007) this is shown in table 7.

IV. CONCLUSION

The INAA technique was used at short-irradiation scheme to determine the vanadium concentrations in crude oils samples collected from seven different oil wells across Niger Delta basin and tar (oil) sands from Okitipupa in Ondo State, the elemental concentration of vanadium in the crude oil ranged from (0.2 – 2.7) μgg^{-1} while the concentration of vanadium in the tar sands was 189.42 ± 28.41 μgg^{-1}. This was very high when compared with values obtained by other workers.This high value of vanadium concentrations can be attributed to the class of the tar sands as being a heavy crude in nature.

REFERENCES

[1]. Annie CJ, Princy SA ans Priya CS (2015) A Review of the Unconventional Methods used for Oil Demetallization of Petroleum Fractions over the Past Decade, Energy and

Fuels, 29(12), 7743-7752, https://doi.org/1021/acs.energyfuels.5b00826.

[2]. Barbooti MM, Al-Taee MA and Qasim BH (2010) Electrothermal Atomic Absorption Sphectrophoto metric Determination of V, Ni and Pb in Hydrocarbon potential soils, Engineer Technology, 28, 17-28

[3]. Bruce EB (1978) Petroleum Industry Analytical Applications of Atomic Spectroscopy, 53-217, https://doi.org/10.1007/1978-1-4684-2589-52.

[4]. Early WB (1969) Porphyrins 464-497, https://doi.org/10.1007/BF012/6320

[5]. Elirich JH, Hilner A and Stark H (1985) Distribution of Trace Elements in Crude oils from Southern Germany; Chemical Geology, 48, 313-323

[6]. Filby RH and Shah KR (1975) Neutron Activation Methods for Trace Elements in Crude oils: In TF Yen (ed) The Role of Trace Metals in Petroleum, Ann Arbor, Michigan.

[7]. Gransch JA and Elsma E (1970) Geochemical Aspects of the Occurrence of Porphyrins in west Venzuelar Mineral Oils and Rocks, 69-86, https://doi.org/10.1016/B978-0-08-012758-3.5-0008-6.

[8]. Kpeglo DO, Darko EO, Akaho EHK, Adu PAS, Abankwah E, Faanu A, Adotey DK, and Opata NS (2015) Trace Element Characterization of Crude oil, Petroleum Products and waste from the Tema oil Refinery in Ghana using Instrumental Neutron Activation Analysis. Elixir Appl. Chem. 84, P33608-33615, www.elixirpublishers.com.

[9]. Milson MF; Montgomery, Brown SR (1966) An Investigation of Vanaldyl Porphyrin Complexes of the Athabasca oil sands vol. 30, No.2, 207-221, https://doi.org/10.1016/0016-7037(66)108-6.

[10]. Mohammad PO, Ikeh BB, Usman BG Ban-Shehu KS and Mikaiwu DA (2013 Determination of Vanadium, Nickel, Copper and Iron as Complexes of Bis-Acetylpivalyl Methane (Ethylene Diamine) in Nigerian Onshore and Offshore oils using HPLC, Journal of Natural Sciences, vol. 13, 8.

[11]. Muhammad SA, Frew RD and Hayman AR (2013) Compound – specific isotope Analysis of Diesel Fuels in a Forensic investigation, in Aris et al, (eds) From sources to solution Springer Singapore.

[12]. Narie WD, Beatriz B, Caleb S and William S (2018) Selenium and Sulphur in Bituminous Sands Mineral and Bitumem Fractions, 224, 718-725, https://doi.org/10.1016/j.fuel2018.03.093

[13]. Ogunleja AS, Alade OS, Odebunmi EO, Amajavu NT and Tshentu ZR (2014) The Ratios of Vanadium-to-Nickel and Phenanthren-to-Dibenzothiophene as means of Identifying Petroleum Source and Classification of Nigeria Crude oils. Published online 2283-2391, Petroleum Science and Technology; 32:19, 2283-2291, D01:10.1080/10916466.2013.795970.

[14]. Ogunsuyi HO, Ajayi OO, Ipinmoroti KO and Oladipupo MOA (2012) NAA of some Nigerian Bitumen samples and their Components. Oriental Journal of Chemistry vol. 28(1) 333-342.

[15]. Oguntimehin and Ipinmoroti KO (2007) Solvent Extraction of Vanadium from Nigerian Bitumen using Tri-Butylphosphate, Journal of Applied Sciences 7, 4028-4031, Do1:10.3923/jas.2007.4028.4031

[16]. Olajire AA Oderinde PA (1966) Finger Printing of Crude oil and their Products. A Review of the Applicability of some Analytical Techniques, Nafta, 47(a), 259-267

[17]. Oluwole AF, Asubiojo OL, Nwachukwu JI, Ojo JO, Ogunsola OJ, Adenumo JA, Filby RH, Fitzgeral S, Grimm C (1993) Radio-Analytical and Nuclear Chem. 168(1) 145-152.

[18]. Qasim YM and Sardasht RT (2018) Journal of Chemical and Pharmaceutical Sciences online 2349-8552, www.jchps.com.

[19]. Robert LL (1959) Petroleum Analytical Chemistry, 31(4), 730-749, https://doi.org/10.1021/ac6014a01z.

[20]. Treibs A (1934) Chlorophyll and Haemin Derivatives in Bituminous Rocks, Petroleum Mineral Waxes and Asphalts. Ann-Chem. 510, 46-62.