

Levels of Heavy Metal in Bonny Light Crude Oil

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Abstract: Levels of Cd, Cu, Ni, V, Pb in Bonny light crude oil was investigated using atomic absorption spectrophotometer. The result revealed mean concentration of Cu (0.0485 ± 0.002 ppm), Ni (0.0375 ± 0.002), V (0.006 ± 0.001 ppm) and Pb (0.093 ± 0.003 ppm). Cd was not detected in the analysis. In a comparison to other crude, the level of these metals was not significantly high. The metal concentration increase on the order: Pb > Cu > Ni > V. level of Pb and Cu were higher than Ni and V possibly as a result of anthropogenic activities. The mean Ni/V ratio was high (6.3) which suggest that the crude oil came from terrestrial derived source rock.

Keywords: Heavy metals, Crude Oil, Ni/V ratio, Bonny, Nigeria

I. Introduction

Crude oil or petroleum is a naturally occurring mixture containing hundreds to thousands of individual chemical compounds [1]. Petroleum may be grouped into broad categories, namely hydrocarbons and non-hydrocarbons. About 90% by weight of the compounds present in petroleum are hydrocarbons. The hydrocarbons present in petroleum may be grouped into three categories, namely: alkanes or paraffins, cycloalkanes or naphthenes and aromatic hydrocarbons [2]. The elemental composition of petroleum varies over the ranges of 82-87% carbon, 11 – 16% hydrogen, 0 – 4% sulphur, 0 – 7% oxygen plus nitrogen and some metals such as nickel, vanadium etc. Elemental analysis of crude oil shows that it contains mainly carbon and hydrogen in the appropriate ratio of six to one by weight [3]. Crude oils are classified as “sweet” or “sour”, based on the low and high sulphur contents of the crude respectively. Crude oil with low sulphur content are classified as “sweet” while those with higher sulphur content are classified as “sour”. Sulphur content is generally considered as undesirable characteristics with respect to processing and end product quality therefore sweet crudes are typically more desirable and valuable than sour crudes [4]. Oil is classified as light and heavy based on American petroleum institute (API) gravity. If oil API gravity is greater than 10, it is higher than water and will float on it. If oil’s API gravity is less than 10, it is heavier than water and will sink [5 and 6]. Lighter crudes are easier and less expensive to produce. They generally have a higher percentage light hydrocarbons that can be recovered with simple distillation at refining. On the other hand, heavy crudes cannot be produced, transported and refined by conventional methods because they have high concentrations of sulphur and several metals, Heavy crudes have density approaching or even exceeding that of water [7].

The metals present in the crude oil include K, Na, Ca, Cu, Pb, Fe, Mg, Na, Mo, Zn, Cd, Ti, Mn, Cr, Co, Sb, U, Al, Sn, Ba, Ga, Ag and As. In general, these elements are present in the crude oils as organic salts (mainly as chloride and sulphate of K, Mg, Na and Ca), and as organometallic compounds of Ca, Cu, Cr, Mg, Fe, Ni, Ti, V and Zn [8]. The determination of metal ions in crude oils has environmental and industrial importance. Analysis of metals in petroleum gives a clue to catagenetic oil formation, maturation of organic matter, correlation, depositional and environmental studies. Metals are important for in the geochemical characterization of crude oil source and origin [9]. The metal ions like vanadium, nickel, copper and iron, behave as catalyst poisons during catalytic cracking process in refining of crude oil. Metals and metalloids may be naturally found in the crude oils and these could be added during production, transportation and storage. However, metals are released in the environment during exploration, production and refining of crude oil [10 and 11]. The metal ions and their ratios have been observed as a valuable tool in oil-oil correction and oil-source rock correlation studies [12 and 13]. It is therefore considered necessary to know the concentration of metals in the oils for meaningful assessment. The aim of this research work is to determine the level of heavy metals (Cd, Cu, Ni, V, and Pb) in Bonny light crude oil.

II. Materials And Method

Sample Collection

The crude oil sample used for this research work was obtained from the NNPC Port Harcourt Refinery, River State, Nigeria. During sampling all bottles were first washed with p-free detergent, rinsed with deionised water and air-dried in accordance with ASTM (2011) [14]. The bottles were later rinsed with the crude oil to be sampled. The sample was prepared using extraction technique whereby the crude oil was extracted with deionized water at the ratio of 10ml crude oil to 1000ml water to obtain water soluble fraction (WSF). The

analysis thus took place by spiking the WSF with the equipment tongue and the values obtained calculated to ppm.

Statistical Analysis

Atomic Absorption Spectrophotometric analysis was done using AAS (Model Buck Scientific VGP-210) to determine the concentration of the Heavy metals in mg/L in the samples following method adapted from [15]. Samples were analyzed in triplicates.

III. Results

Table 1: Mean Concentration of Heavy Metals in bonny Light Crude

| Heavy metals (ppm) | Test 1 | Test 2 | Test 3 | Wavelength (nm) | Mean |
|--------------------|--------|--------|--------|-----------------|----------------|
| Cadmium (Cd) | ND | ND | ND | 288.9 | ND |
| Copper (Cu) | 0.045 | 0.048 | 0.052 | 324.8 | 0.0485 ± 0.002 |
| Nickel (Ni) | 0.038 | 0.037 | 0.037 | 232.0 | 0.0375 ± 0.002 |
| Vanadium (V) | 0.006 | 0.006 | 0.006 | 318.4 | 0.006 ± 0.001 |
| Lead (Pb) | 0.093 | 0.096 | 0.090 | 283.3 | 0.093 ± 0.003 |
| Ni/ V ratio | 6.3 | 6.2 | 6.3 | | 6.3 |

IV. Discussion

Table 1 shows that metal concentration increase on proceeding order: Pb > Cu > Ni > V > Cd. All the metals found in this oil were also found in similar Nigerian crude by other researchers [16]. Low levels of metal were observed for all the investigated metals. This agrees with reports that light crude oil samples usually contain relatively low trace metal contents compared to the heavy crudes [18]. The level of Pb and Cu were higher than Ni and V contrary to the general observations [17]. This could be as a result of the anthropogenic activities of man such as extraction, storage and transportation which could contaminate the oil. This is aside, original metals incorporated in oil as metal complexes during catagenesis stage of fuel formation [18]. It has been reported that most soils associated with the areas where crude oil is found in Nigeria are also associated with appreciable deposits of metal ores [19]. Mean Ni/V ratio was found to be 6.3 and this was lower than those reported by [20]. Inverse of Ni/V ratio is used to in the determination of source rock type, depositional environment and maturation of crude oil [21]. Ni/V ratio increase as maturation of crude oil increases and high Ni/V suggest terrestrial derived source rock [21]. Nickel and vanadium adversely affect both the selectivity and activity of catalysts and they have the potential to corrode refinery equipment at high concentration

V. Conclusion

This work showed that the concentration of heavy metals in Bonny light crude were low like other investigated Nigerian crudes. Higher levels of Pb and Cu were observed than those of Ni and V possibly as a result of anthropogenic activities such as extraction, storage and transportation. The mean Ni/V ratio was high (6.3) which suggest that the crude oil came from terrestrial derived source rock.

References

- [1]. Ekweozo, C.M, Okojun, J.I; Ekong, D.E. and Maxwell J.R (1988). Preliminary Organic Geochemical Studies of Samples from the Niger delta. Part 1: Analysis of Crude oils for Triterpenes. *Chem Geology* (27): 11-28.
- [2]. Odebunmi, O. And Adeniyi, S .A (2007). Infrared And Ultra Violet Spectrophotometric Analysis Of Chroma Tographic Fractions Of Crude Oils And Petroleum Products. *Bull. Chem. Soc. Ethiop.* 21(1),135-140.
- [3]. Akpan, I.O.(2005). Effect of sample treatment on trace metal determination of Nigerian crude oils by Atomic Absorption Spectroscopy (AAS) Technique. *African Journal of environmental pollution and health.* 4(2):1-5.
- [4]. Abdulkareem, A.S., Kovo, A. S. (2006). Simulation of the Viscosity of Different Nigerian Crude Oil. *Leonardo Journal of Sciences.* 8: 7-12.
- [5]. American Petroleum Institute (2011). API Specification for Materials and Testing for Petroleum Products. API Production Dept. API 14A, Eleventh edition. Dallas: 20-21. AOAC (1984) Official Methods Analytical Chemistry 10th ed: 79-81
- [6]. Olajire A. A. and Oderinde, R. A. (1992). Trace metals in Nigerian crude oils and their heavy-end. Distillates *Bulletin of the Chemical Society of Japan.* pp
- [7]. Ahmad, H., Tsafe, A.I., Zuru, A. A., Shehu, R. A. ., Atiku F. A and Itodo A. U. (2010) Physicochemical and Heavy Metals Values of Nigerian Crude Oil Samples. *International Journal of natural and applied Science* 6(1): 10-15
- [8]. Ali, M. F., Bukhari, A. and Saleem, M. (1983). Trace metals in crude oils from Saudi Arabia. *Ind. Eng. Chem. Prod. Res. Dev.*, 22: 691-694,
- [9]. Ellrich, J., Hirner, A and Stärk, H. Distribution of trace elements in crude oils from southern Germany, *Chem. Geol.* 48 (1985) 313–323.
- [10]. Gagram, (2002). Fuel gravity, density and weight. Source: <http://www.gammontech.com/gg19htm>
- [11]. Barwise, A. J. G. (1990). Role of nickel and vanadium in petroleum classification. *Energy and Fuels*, 4, 647-652.
- [12]. Osuji, L.C. and Anita B.S. Geochemical Implications of some Chemical Fossil as Indicators of Petroleum Source Rocks. *Journal of Applied Science and Environmental Management* 2005; 9(1):45-49.
- [13]. Oderinde, R. A. (1984). Studies on Nigerias Petroleum Part 1. Varietal Differences In Vanadium and Titanium Contents. *Nigerian Journal of Sciences* 18:143-145.
- [14]. ASTM- American Society for Testing and Materials (ASTM) Standard C33 (2011). Standard Test Method for substances in Crude Oil. ASTM International, West Conshohocken, PA, 2011, DOI: 10.1520/C0033-03, www.astm.org. Annual Book of Standards. Vol. 2: 287, 97, 93, 445.

- [15]. Hardaway, C., Sneddom, J. and Beck, J. N. (2004). Determination of metals in crude oil by atomic spectroscopy. *Analytical Letters*, 37(14): 2881-2899.
- [16]. Akpoveta, O.V. and Osakwe S.A. (2014) Determination of Heavy Metals Content in Refined petroleum products, *Journal of Applied Chemistry*, Vol. Issue 6, pp 01-02
- [17]. Udeme J.D., Etim I. U. (2012) Physicochemical Studies Of Nigeria's Crude Oil Blends, *Petroleum & Coal* 54 (3) 243-251
- [18]. Dusseault, M.B. (2001). "Comparing Venezuelan and Canadian Heavy Oil and Tar Sands". Calgary, Canada: Canadian International Petroleum Conference. pp 1-9
- [19]. Udoessien, E.I. (1997): Pollution in Petroleum and Allied Industries. Mef (Nig) Ltd,Uyo: 5-7.
- [20]. Owamah H.I (2013) Heavy Metals Determination and Assessment in a Petroleum Impacted River in the Niger Delta Region of Nigeria, *J Pet Environ Biotechnol*, 4(1) 1-4
- [21]. Onajake M.C., Oforka N.C., and Osuji L.C. (2011) Trace Metals Geochemistry of Crude Oils from Umutu/Bomu Fields in South West Niger delta Nigeria, *Energy and Environment Research*, Vol 1, No 1, pp 139-146