Trace Elemental Analysis of Nigerian Petroleum Products Using AAS Method

Nafi'u Tijjani, P.O Ike, B.B Usman, D. I. Malami and Alaere Matholo

Abstract - Some physico-chemical analysis of samples of Gasoline, Kerosene, Diesel Oil, Low Pour Point Oil and Residual fuel have been studied. The samples were also analyzed for trace elements. The results confirmed that Heavy distillates fractions(Residual fuel and LPFO) contains trace metals higher than the distillates fraction(Automobile Gas Oil or Diesel) followed by intermediates (Dual Purpose Kerosene) and lights ends fractions(Premium Motor Sprit / Gasoline). The samples were analyzed by gravimetric and micro-kjeldahl methods for sulphur and nitrogen content respectively. The experiment data indicated that, the total sulphur and nitrogen contents increased from light ends, intermediates, distillates to heavy distillates fractions and also the concentrations of the trace metals in the petroleum products follows the same trend i.e. from less viscous petroleum products (Gasoline, Kerosene and Diesel Fuel) to high viscous petroleum products sample (residual fuel and LPFO) . The results were discussed in terms of effects of this impurities on the refinery process.

Keyword: Ashing Method, Pour Point, Specific Gravity, Sulphur Content, Trace metals, Gravimetric and micro-kjeldahl methods.

1. INTRODUCTION

Crude oil and its finished products (Petroleum Products) contains mainly hydrocarbons especially alkanes, naphthenic and aromatics hydrocarbons[1]. It contains also some nitrogen, oxygen and sulphur containing compounds along with trace amounts of elements especially nickel, vanadium , cadmium, iron etc.[2,3] The presence of trace metals and non-metals in the crude oil and petroleum products is destructive, especially in a refining process. This may adversely affect both the processing equipment and storage facilities of the petroleum refinery. The presence of sulphur compound in the finished petroleum products influence the colour, odour, stability and storage facilities of the finished petroleum products4.Various analytical methods have been reported for the determination of trace metals in petroleum products. Traces of iron, nickel, and vanadium in petroleum products were analyzed using spectrophotometry method. The sample was ashed and taking up with the potassium bisulphate. The measurement were based on the development of coloured solutions by reagents specific for each elements[5]. Henry and George, 1975 employed AAS to determined heavy metals in petroleum products[6]. They used two methods which are based on the decomposition and cold water vapour atomic adsorption. Another method involved acid decomposition of the samples in a closed system while the other method used oxy-hydrogen combustion to decompose the sample.

In another report, Winston and Harry,1975 used AAS to determine trace quantities of cadmium in petroleum and petroleum products in which the sample was digested with sulphuric acid and then ashed[7]. In another report, Oderinde,1984 determined the vanadium and titanium contents of nine Nigerian crude and petroleum products using a spectrometric method[8] He reported that in some of the samples the Vanadium and Titanium content were high enough to cause corrosion in turbines and refining processes line in the refinery. In a recent study,Anthony,2005 reported in his comprehensive analysis of various metallic elements in Nigerian petroleum products using Atomic Absorption Spectroscopy technique, he discuss the influence of these trace metals contaminants in refinery processes[9].

Farroha et, al,1984 used electrochemical method to determine trace levels of sulphur in petroleum by constant current coulometry. The Tandem mass spectrometer combined with chemical reaction was used to concentrate sulphur containing poly-nuclear aromatic compound by wood et al,[9].Oderinde, 1984 thoroughly investigated the types of sulphur compounds present in Ugheli Quality Control Centre(UQCC) of crude oil distillates fractions. The total nitrogen was in petroleum fractions was determined using the modified Kjedahl method [13,14] The total nitrogen contents of the twenty eight Nigerian well head crudes and their fractions were quantitatively measured by a by coloumetric technique by Nwadinigwe and Maduka[14].

2. EXPERIMENTAL

2.1 MATERIALS

The Petroleum Products sample used in this research paper were Gasoline, Kerosene, Diesel Oil, LPFO and Residual Fuel obtained from Kaduna Refining and Petrochemical company limited, a subsidiary of NNPC, Nigeria.

2.2 CHEMICALS/REAGENTS

All the chemicals and reagents used in this study were of analytical grades, the glass wares used were cleansed, rinsed with distilled water and air dried. Physicochemical parameters of petroleum products understudy;

2.3 THE PHYSIC-CHEMICAL PROPERTIES WERE DETERMINED BY ASTM AND IP METHODS AS FOLLOWS:

a) The density, Specific Gravity and API gravity were determined using ASTM method [17,18]. The specific gravity determination involves weighing (W_1) a known volume of a sample in a density bottle at certain temperature and weighing W2 an equal volume of water in the same density bottle at the same temperature. The specific gravity is the ratio of the two weights W_1/W_2. The API gravity of the sample was then calculated by using the equation[18].
API = 141.5/S.G – 131.5 ----------.(1)
Where S.G means Specific Gravity of the Sample.

b) Viscosity Determination follows the IP method[21] .This involves measuring the time of flow of the sample between two marked points on the Ostwald viscometer and calculating the viscosity by using the standard equation.

c) The Aniline point determination involves heating sample in a test tube until the two phases become miscible. The mixture was then cool at a controlled rate and temperature was monitored. The minimum temperature at which the two phases separate was taken as the Aniline point [19]

d) The pour point determination involved heating the sample in a test followed by cooling in a cooling bath at a controlled rate. The pour point is the lowest temperature at which there is a loss of fluidity in the sample[20].

e) The water content determination follows the I.P method by using the Dean and Stark apparatus[19] .

2.4 TRACE METAL CONTENT:

The procedure involved Ashing 10g of the petroleum products sample already placed on a porcelain crucible at 500 ^{0}C in a muffle furnace for 1.5 hours. When the Ashing was completed , the residue was gently wormed with 10 cm3 of 0.02 M Nitric acid to facilitate the complete extraction of the trace metals from the sample, a glass rod was used to stir and crushed all the acid soluble elements in the ashes. The slurry was then filtered into a 100 ml volumetric flask, and the residue was filtered into 100 ml volumetric flask, and the residue was further washed with 10ml of 0.02 M Nitric acid solution. This was then diluted with distilled water to the mark. The solution was then analyzed using atomic absorption spectrophotometer[20,22]. The metal content of petroleum products were determined using 305B atomic absorption spectrophotometer attached to graphite atomizer and a HP 960C Computer Printer, the instrument determined the concentration of the trace metals in mg/l in the samples.

2.5 TOTAL SULPHUR CONTENT:

The procedure involved weighing 1.5g of the petroleum products sample into 500 ml round bottomed flask and adding 250ml of distilled water to it. Then 5g of solid KOH and 15g of solid $KMnO_4$ were weighed and added to the mixture in the flask together with anti-bombing chips. The mixture was refluxed for 6 hours and allowed to cool then 150ml of the concentrated HCL was added slowly through the condenser. The flask was heated until its contents turned colourless, cooled and the condenser washed into the flask with a little distilled water. The content of the flask with a little distilled water. The content of the flask was collected into a 500ml beaker washed with distilled water and filtered into a beaker. The filtrate was boiled with 10ml of Concentrated HCL and 100ml of hot barium chloride with stirring. This resulted in deposition of a fine white precipitate of barium sulphate after heating the beaker on the water bath for 5hr. the precipitate was filtered and washed with hot distilled water to remove chloride ions. The filter paper containing the precipitate was deposited on a weighed small porcelain crucible and heated strongly on a hot plate until a white powder was left. A drop of concentrated HCL and a drop of concentrated H2SO4 were added and the crucible was reheated until a white powder was left

Calculation:

Mass of $BaSO_4$ precipitated, mB (g) = (Mass of $BaSO_4$ in the sample – mass of $BaSO_4$ in the blank) Gravimetric factor of $BaSO_4$ = 0.137

Mass of sulphur in $BaSO_4$ precipitated (mS) = 0.137g × mass of mB

Mass of sampled analyzed = 1.5g

$$\% \text{ sulphur} = \frac{ms}{1.5g} \times 100 = \frac{0.137 \times mB}{1.5g} \times 100$$

powder was left. The crucible was cooled and weighed and the weight of barium sulphate determined by difference.

2.6 TOTAL NITROGEN CONTENT:

The procedure involved weighing 1g of petroleum product sample into a round bottomed flask. Then 5g of Na_2SO_4 was added followed by the addition of 0.23g of $CuSO_4$ and 12.5ml of concentrated H_2SO_4, the mixture was heated to a temperature below the boiling point of the acid until the digestion was completed and digest turned green and clear. The flask and the content were then allowed to cool and the solution transferred into a 250ml standard flask. A 5ml

portion of each digest was pipetted into a micro-Kjeldahl unit and an excess of 40% aqueous NaOH was added to make the solution strongly alkaline and force ammonia out of the solution. The ammonia was distilled into 5ml of the prepared boric acid indicator in a titration flask containing about 45ml of distillate which contains ammonium borate. The borate anion was titrated with 0.01M HCL to regenerate the bluish color of the boric acid at the end point.

3. RESULTS AND DISCUSSION

Table1: Physico-chemical results

Parameters:	Unit	PMS	DPK	AGO	LPFO
Density :	kg/m	0.7528	0.8220	0.8712	0.9189
Specific G:	kg/l	0.8432	0.8404	0.8595	0.9528
API Gravity:	Unit	36.3	36.9	33.1	22.5
Total Sulphur:	%W	0.03	0.04	0.16	0.41
Flash Point:	^{0}F	N.A	130.6	209.6	248
Kinematic V.	cs.t	3.12	5.10	6.19	16.3
Viscosity:	Unit	0.8200	0.9900	1.40	7.99
Pour Point:	^{0}F	+3	+2	-3	-5
Water content:	%Vol.	0.01	0.03	0.10	0.08

Table 2: Concentration of Trace Metals

Elements	Cu	Zn	Mn	Si	V	Mo	Fe
Blank :	0.06	0.18	0.86	0.12	0.09	0.04	0.26
PMS:	0.64	1.58	1.28	0.72	0.58	0.46	1.48
DPK:	0.26	0.48	1.04	0.28	0.18	0.11	1.28
AGO:	1.06	1.50	1.46	0.84	0.45	0.54	1.74
LPFO:	3.65	4.70	6.6	4.70	2.9	3.65	5.40
R/F:	3.25	4.20	4.8	3.9	2.4	3.10	4.75

4.Discussion

4.1 PHYSICO-CHEMICAL PARAMETERS; The results of the analysis of physicochemical properties of petroleum products are contained in Table 1. the data showed that the values of density, specific gravity, viscosity, kinematic viscosity of petroleum products assayed increase from light fractions to heavy fractions of petroleum distillates. The API gravity of light fractions is above 30^0 while that of heavy fractions is below 30^0. Furthermore, as expected, the pour point and flash point of light fractions is higher than that of heavy fractions. The data also show that Gasoline has a 0.01% water by volume, while Kerosene, Diesel and LPFO have 0.03, 0.05 and 0.08% water by volume respectively. The higher pour point and flash point of LPFO and Diesel fuel over Gasoline and Kerosene is probably due to the higher water content in Diesel and LPFO.

The metal content of Nigerian petroleum products are shown in Table 2. The data showed that the metal contents increase on proceeding from light to heavy petroleum distillates (Gasoline > Kerosene > Diesel > LPFO > Residual fuel). It is observed from the results that the metal contents vary with the viscosity of the petroleum products. The nature of this metals and the abundance in petroleum products may probably provides information on the origin, migration and maturation of raw material of these petroleum products as well as indicating the regional geochemical prospecting base as well as the processing and storage channels in the refinery. As a rule, the metal content increase with viscosity of these petroleum products (i.e. the heavier the petroleum product the higher its metal contents) consequently, the lighter distillates contain less metal contents.

The metal contents of the Nigerian petroleum products in the literature show a wide variation. For example Anthony,2005[23], imported iron content in the range of 10.94- 25.0 ppm while our results show the range of 0.25 – 4.75 mg/l. The wide variation is possibly due to the combination of several factors including the type of petroleum refining equipments (because some of them are made up of different percentage of metallic alloys), sample handling procedures and different analytical techniques adopted. The metal contents of Nigerian petroleum products are in general lower than those of petroleum products from other regions of the world. The report of Adolfo, *et, al*., 2007[24], for example show that iron contents of 12.39ppm , 725 mg/kg and 113.2 ppm for petroleum products from Central American Region (USA), Mexico and Venezuela respectively. However , even as this low levels, the metal contents of Nigerian petroleum products, and especially of vanadium, cadmium, cupper, and iron, is high enough to cause corrosion of turbines distillation towers, etc according to Oderinde,(1984). The data in Table 1 shows that the weight percentage of total sulphur in various

petroleum products, the data fall within the range for sulphur expected in Nigerian crude oils and petroleum products, i.e. 0.05 – 0.30 w/%[4, 10, 25]. It can be seen from Table 1 that Gasoline, (light ends fraction), Kerosene (Intermediate fraction), Diesel fuel (Distillates), LPFO and Residual fuel (heavy distillates) contain 0.03, 0.04, 0.16 and 0.41 W/% sulphur respectively.

4.2 TOTAL NITROGEN CONTENT

The percentage nitrogen in the sample is calculated by using the equation:

$$\% \text{ Nitrogen in the sample} = (0.01 \times 0.014)\text{g } N_2 \times \frac{250}{5} \times \frac{100 \times t}{W}$$

Where t= titre value of 0.01M HCL used in the titration.
w= weight (g) of the sample taken for the analysis

The experimental data in Table 2 show the weight percentage of total nitrogen in various spetroleum products. These value falls within the range of nitrogen normally reported for Nigerian crude oils and petroleum products. Furthermore as expected, the weight percentage of nitrogen of heavy LPFO and residual fuel is higher than that of gasoline, kerosene and diesel oil. This difference may depend on the source, process, conditions and the final treatment of the petroleum products in the refining industry.

The nitrogenous compounds in petroleum products are important impurities because they have deleterious effects on the quality of finished products and the environments. They poison cracking and reform catalysts during petroleum processing, cause instability of finished products, promote sediment and gum formation and impact color and odour. The combustion of liquids fuels containing nitrogenous compounds produces oxides of nitrogen which are the potential health hazards.

Nwadinigwe and Maduka carried out a detailed analysis of total, basic and non basic nitrogen contents of 28 Nigerian well head crude's and their fractions. Our data for petroleum products agree reasonably well with Nwadinigwe and Maduka's data for petroleum distillate fractions showing the necessity for denitrogenation.

5 CONCLUSION

This work showed that Nigerian petroleum products contains trace amount of Cu, Zn, Mn, Si, V, Mo, Fe . The presence or absence of some elements in Nigerian petroleum products may be link to the chemical and geological origin of its raw materials and also industrial process and the transportation method adopted. Hence the concentrations of trace and heavy elements in Nigerian petroleum products may reveal information on the environmental friendliness and quality of petroleum products and probably give an idea of the sources of these trace heavy metals in the petroleum industry. It was obvious from this study, the Nigerian petroleum products analyzed have low metals contents especially in petrol, kerosene and gas oil sample. However, despite the low concentrations, they could still lead to serious health hazard considering their cumulative effects in the environment.

REFERENCE

1.Gruse, W . A . and Stevens , D. R. (1960), Chemical Technology of Petroleum. Mc Graw Hill Book Co. Inc New York 675.

2. Singh P. P., Joseph T. M., and Dhavale. R. G. (1983) College Industrial Chemistry. 4th edition Himalaya publishing house Bombay 174 – 197.

3. Olajire A. A. and Oderinde R. A. (1996), "Fingerprinting" of crude oil and their products. A review of the applicability of some analytical techniques. Nafta 47 (9)259 -267.

4.Oderinde R. A. (1989) Studies on Nigerian Petroleum ; Part 2 : Nature and Distribution of Sulfur Compounds in UQCC crude and the Comparative evaluation with selected Middle East crudes , Nigeria Journal of Science 23 (1 & 2) 64-68.

5. France. M. W. (1964) "Determination of Fe, Ni and V in Petroleum Oils", Anal Chem 21 (12) 1543

6. Henry E. K. and George . E. M. (1975) Analysis of petroleum for trace metals (1) Determination of Hg in petroleum products. Anal Chem 47, 1263

7.Winston, K. R. and Harry, H. W. (1975). "Analysis of Petroleum for trace metal (11) : Determination of trace quantities of cadmiumin in petroleum by ASS" Anal Chem. 47 1269

8) Oderinde R. A. (1984) Studies on Nigerian Petroleum Part 1; Vertical Difference in the Vanadium and Titanium content. Nigeria Journal of Science Vol. 18, 143 – 145

9.Nwadinigwe C. A. and Nworgu O. N. (1999): "Metal contaminants in some Nigerian well-head crudes : Comparative Analysis". J. Chem. Soc. Nigeria 24,118 – 121

10. Farroha , S. M., Habboush, A. E., and Michael, M. N. (1984) , "Determination of milligram amounts of sulfur in hydrocarbons by constant current coulometry" Anal Chem. 56 (7) 1182 – 1183

11.Wood, K. V. Cooks, R. G. Laugal, J. A. and Benkeser , R. A. (1985), Combination of chemical reduction and Tandem Mass spectrometry for the characterization of sulphur-containing fuel constituents,Anal. Chem. 56(7),1182 - 1183.

12. Snell- Eltre(1971) encyclopedia of industrial chemistry analysis, John Wiley and sons. Newyork, 16,449-466

13.Annaual book of ASTM Standard(1985), 05,03, D 3228-3283

14 Nwadinigwa C. A. and Maduka M. C (1993) A quantitative assessment of the classes of nitrogenous compounds light crudes. Fuel 72 (8), 1139-1143

17. Annual book of ASTM standard(1985), standard test method for density, relative density(specific gravity, and API gravity of crude petroleum and liquid petroleum products by hydrometer method) 05.01,D1298-80,646-649

18. a)Institute of petroleum(1987) " method of analysis and testing of petroleum and related products" vol 2, 262-378, John Wiley and sons ltd, London
19. Institute pf petroleum(1987) " methods of analysis and testing of petroleum and related products. Vol 1, 18-126, John Wiley and sons limited

20 b)Institute of petroleum(1987)" methods for analysis and testing of petroleum and realated products: kinematic viscosity of transparent and opaque liquids and the calculation dynamic viscosity" vol 1,1-17. John Wiley and sons limited, London]

21. Milner, B. A. and Whiteside, P. J. (1986) " Introduction of atomic absorption spectrophotometric", Pye unicam limited, Cambridge, UK, 69-70

22. Vishnoil, N. K.(1979) " Advanced practical organic chemisitry" , first edition reprint. Vikas. New Delhi, 424.

23. Anthony S.B,2005,Analytical evaluation of trace metals components of the Nigerian petroleum products by AAS, M.Sc thesis submitted to UDUS, Pp 54.

24.Adolfo Fernandez, Aisha Singh, Rudolf Jaffe,2007,A literature review on trace metals and organic compounds of anthropogenic originin the Caribbean region, Journal of international for marine environmental scientist, engineering, administration, politiceans, and lawyers, volume 54,issue 11
25. Adegbite,. O. A.(1989),Determination of sulphur and nitrogen contents of some Nigerian coal and crude oil samples, a technical paper presented to NNPC.32.