Abstract - In this research, some selected trace metals in atmospheric and vacuum oil residue were determined and compared. A total of ten Oil residue samples were used in this study, five each from atmospheric and vacuum distillation, the samples were obtained from Kaduna Petroleum and refining petrochemical company (KRPC), Kaduna, Nigeria. The samples were characterised by AAS. The result of AAS analysis Shows that lead (Pb) was not detected in all the samples for both residues also Nickel (Ni) was not detected in all the samples for atmospheric residue but detected in some sample of vacuum residue. The concentration (ppm) levels of these elements in the residue fractions analysed for atmospheric residue ranges from 2.097 - 0.257 for Chromium (Cr) and 3.083 - 0.63 for Iron (Fe) while vacuum residue ranges from 2.656-0.136 for Nickel (Ni), 1.509 – 0.004 for Chromium (Cr) and 66.745 -0.0392 for Iron (Fe). Atmospheric and Vacuum residue samples analysed have shown low metal content, despite the low concentration, they could still lead to serious health hazard considering their cumulative effects in the environment.

Key words - Atomic Absorption Spectroscopy, Heavy Metals, Atmospheric residue, Vacuum residue.

I. INTRODUCTION

Petroleum/crude oils are naturally occurring, complex mixtures of hydrocarbons with varying amounts of sulfur, oxygen and nitrogen, as well as trace amounts of metals such as nickel and vanadium. Chemical and physical compositions vary with the origin and age of the crude oil [1]. The occurrence of metallic constituents in crude oil is of considerably greater interest to the petroleum industry than might be expected from the very small amounts present [3]. Even minute amounts of iron, copper, and particularly nickel and vanadium in the charging stocks for catalytic cracking affect the activity of the catalyst and result in increased gas and coke formation and reduced yields of gasoline. In high-temperature power generators, such as oil-fired gas turbines, the presence of metallic constituents, particularly vanadium in the fuel, may lead to ash deposits on the turbine rotors, thus reducing clearances and disturbing their balance [2]. More particularly, damage by corrosion may be very severe. The ash resulting from the combustion of fuels containing sodium and especially vanadium reacts with refractory furnace linings to lower their fusion points, and so cause their deterioration [4].

This study is aimed at investigating and comparing the concentration level of Pb,Cr, Fe and Ni in residual fractions of Nigerian Crude oil and this will help in assessing the impact of Nigerian crude oil on environment.

II. MATERIALS AND METHODS

The petroleum products used in this research work were residues from atmospheric and vacuum distillation obtained from Kaduna Refining and Petrochemical company (KRPC), a subsidiary of NNPC, Nigeria.

III. REAGENTS

All the reagents used in this work are of Analytical grade.

IV. SAMPLE COLLECTION

Ten Crude oil Residues samples were collected from oil movement unit of Kaduna Refining and Petrochemical company (KRPC), a subsidiary of NNPC. 2L of each oil were obtained, the samples were put in a clean sample bottles and kept away from sunlight... Atmospheric residue samples were collected first from the same pool and Vacuum Residue Samples were then collected a week later.

a. Treatment of sample for AAS analysis:

The procedure involved Ashing 10g of sample already placed on a porcelain crucible at 500°C in a muffle furnace for 1.5 hours. When the Ashing was completed, the residue was gently warmed 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 lumps. The content was then filtered into a 100cm³ volumetric flask, and the residue was further washed with 10cm³ of 0.02 M Nitric. This was then diluted with distilled water to the mark and repeated for all the ten samples.

b. AAS analysis:

The spectrophotometer (AAnalyst 400 by Shimadzu, JAPAN) was being set up in accordance with the manufacturer’s instructions for each element to be analysed. The blank and the samples were aspirated into the flame and their concentrations in ppm recorded and this was done in triplicate.
The concentration of each analyte (X) in the sample was calculated using the equation

\[ X \left( \frac{mg}{100g} \right) = X (ppm) \times \frac{\text{Volume of aliquot}}{\text{weight of sample}} \times 10 \]

V. RESULTS

Table 1.0: Concentration of Heavy Metals in Atmospheric Residue by AAS Method

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ni</th>
<th>Pb</th>
<th>Cr</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>NDT</td>
<td>NDT</td>
<td>1.911±0.079</td>
<td>0.979±0.014</td>
</tr>
<tr>
<td>A</td>
<td>NDT</td>
<td>NDT</td>
<td>2.097±0.078</td>
<td>0.636±0.057</td>
</tr>
<tr>
<td>A</td>
<td>NDT</td>
<td>NDT</td>
<td>0.315±0.033</td>
<td>3.083±0.026</td>
</tr>
<tr>
<td>A</td>
<td>NDT</td>
<td>NDT</td>
<td>0.358±0.025</td>
<td>1.716±0.131</td>
</tr>
<tr>
<td>A</td>
<td>NDT</td>
<td>NDT</td>
<td>2.57±0.017</td>
<td>2.912±0.059</td>
</tr>
<tr>
<td>Range</td>
<td></td>
<td></td>
<td>2.097 – 0.257</td>
<td>3.083 – 0.636</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>0.9876 ± 0.047</td>
<td>1.8652 ± 0.057</td>
</tr>
</tbody>
</table>

Results were presented as mean ± standard deviation of triplicate analysis

Key: A = Atmospheric oil residue
NDT = Not detected

Table 2: Concentration of Heavy Metals in Vacuum Residue Sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ni</th>
<th>Pb</th>
<th>Cr</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>2.322±0.136</td>
<td>NDT</td>
<td>0.923±0.031</td>
<td>1.187±0.032</td>
</tr>
<tr>
<td>V</td>
<td>2.656±0.259</td>
<td>NDT</td>
<td>0.0408±0.055</td>
<td>0.392±0.022</td>
</tr>
<tr>
<td>V</td>
<td>NDT</td>
<td>NDT</td>
<td>1.26±0.073</td>
<td>66.745±0.071</td>
</tr>
<tr>
<td>V</td>
<td>1.245±0.139</td>
<td>NDT</td>
<td>1.509±0.059</td>
<td>4.257±0.063</td>
</tr>
<tr>
<td>V</td>
<td>NDT</td>
<td>NDT</td>
<td>1.403±0.047</td>
<td>6.863±0.275</td>
</tr>
<tr>
<td>Range</td>
<td>2.656 – 1.245</td>
<td></td>
<td>1.027 - 0.053</td>
<td>66.745 – 0.392</td>
</tr>
<tr>
<td>Average</td>
<td>1.245±0.106</td>
<td></td>
<td>1.027±0.053</td>
<td>15.888±0.092</td>
</tr>
</tbody>
</table>

Results were presented as mean ± standard deviation of triplicate analysis

Key: V = Vacuum oil residue
NDT = Not detected

VI. DISCUSSION

AAS is an analytical technique that measures the concentration of an element by measuring the amount of light (intensity of light) that is absorbed at a characteristic wavelength when it passes through a cloud of atoms of this element, as the number of atoms in the light path increases, the amount of light absorbed increases in a predictable way. AAS was adopted in this research work for determination of concentration of metals because of its high sample resolution, simplicity, high precision and accuracy.

Result of the AAS Analysis are summarized in Table 1 and 2 above; The result shows that for atmospheric residue samples, Fe > Cr, While For Vacuum Residue Samples, Fe > Ni > Cr and lead (Pb) was not detected in both the residual samples, also Nickel was not detected in all the atmospheric residue samples and two samples of Vacuum residue. The result shows that Iron (Fe) had the highest concentration and Chromium had the least concentration. The order shows a slight difference in the distribution of the heavy metals in the samples. These may be connected to difference in the distribution in geological activity and mineral accumulation during rock deposition. The knowledge of metal contents of an oil sample has been essential information for the sake of designing of demetallatin process and evaluating its effectiveness [7]. Also, The mean Iron concentration in atmospheric residue Samples ranges from 3.083 – 0.636 ppm averaging 1.8652±0.057 and 66.745 – 0.392 ppm averaging 15.888±0.092 for Vacuum Residue Sample. This shows a significant difference in the iron levels of the two residual...
Samples. These values are very low compared to 43 to 110 ppm found in some Nigeria, Western Canada, Saudi Arabia and Venezuelan Crude’s [2,6]. The mean Chromium Concentration in atmospheric residue samples ranges from 2.097 ± 0.057 averaging 0.9876 ± 0.047 and 1.027 ± 0.053 averaging 1.027 ± 0.053 for Vacuum residue Samples. This shows an insignificant difference in the chromium level of the two residual samples. The result agreed with the concentration of chromium as earlier reported in some western Canada, Saudi Arabia and Italian Crude oil having range of 0.09-10.70 ppm [7]. The mean Nickel Concentration of atmospheric residue samples were not detected while the mean Nickel concentration of Vacuum residue samples detected ranges from 2.656 ± 1.245 averaging 1.245 ± 0.106. These value shows a significant difference in the Nickel level of the two residual samples. The result shows a lower concentration of Nickel as earlier reported in some Nigerian, Saudi Arabian, Italian and Venezuela crudes having a range of 5.0 -111 ppm([6],[5]).

The difference in concentration of the metals is possibly due to several factors including the type of petroleum refining equipment, sample handling procedure and different analytical techniques adopted. It is obvious from this studies and previous ones that Nigerian crude oil residue have low metals contents, despite the low concentration, they could still lead to serious health hazard considering their cumulative effects in the environment.

VII. CONCLUSION

Atmospheric and Vacuum residue samples analysed have shown low metal content, despite the low concentration, they could still lead to serious health hazard considering their cumulative effects in the environment. The presence or absence of these elements in Crude oil residue is linked to its Chemical, Vegetative and Geological Origin.

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REFERENCES