OPTIMIZATION OF HYDROCARBON RECOVERY BY ENHANCED COLUMN CHROMATOGRAPHY

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Abstract
Four sediment samples collected from Ethiope River in Ethiope East Local Government Area of Delta State, Nigeria and eighteen different column packing ratios of silica gel and alumina were used in this investigation. The variation of the composition of the stationary phase (Silical gel and alumina, SA) gave different yields of aromatic and saturated hydrocarbons. In all the sediments, the SA(1:2) column length ratio eluted the highest amount of saturated hydrocarbons; sediment 1, 287ppm; sediment 11, 347ppm; sediment 111, 320ppm and sediment 1V, 337ppm with a mean of 322.15±8.5ppm. The modified SA (2:1) i.e. MSA(2:1) column length ratio eluted the highest amount of aromatic hydrocarbons, 119ppm for sediment 1; 110ppm for sediment 11; 123ppm for sediment 111 and 90ppm for sediment 1V with a mean of 110.5±18ppm. The modified AS2:1 i.e. MAS(2:1) weight ratio eluted the least amount of saturated hydrocarbon, sediment 1, 22.9ppm; sediment 11, 19ppm; sediment 111, 30ppm and sediment 1V, 20ppm with a mean of 23.0±6.1ppm while the SA1:1 weight ratio ratio eluted the least amount of aromatic hydrocarbon, sediment 1, 8ppm; sediment 11, 3ppm; sediment 111, 7.6ppm and sediment 1V, 12ppm with a mean of 7.7±4.5ppm. The differences in elution between the column length ratio and column weight ratio was statistically significant at P≤0.05. Therefore, modification of analytical procedures may at times lead to optimized outcomes. These differences in the yields of the aromatic and saturated hydrocarbons are due to the differences in the relative adsorption of the aromatic and saturated hydrocarbons on the stationary phase and the moderating influence of the components of the stationary phase on each other.

Key words: Ethiope river, column length ratio, weight ratio, elution, optimization.

Introduction
Generally, industries produce wastes which are either deliberately or accidentally dumped into water basins and land. Most of the wastes contain pollutant metals and organic compounds which ultimately form part of the sedimented matter in the water bodies. A build-up of these pollutants would become poisonous to aquatic life and subsequently to man that depends on them for livelihood [1].

In Ethiope East, Delta State, Nigeria, the major industrial activity is lumbering and processing of woods utilizing different machineries operating on fossil fuel. Hydrocarbons are known to be the major components of fossil fuels [2] and their presence in the sediment above regulatory consent limits indicates pollution.

There are also incessant cases of oil pipeline rupture and leakages in the adjoining Jesse and Kokori towns. These expose the aquatic environment of Ethiope River to excess load of these hydrocarbons [3]. From the environmental standpoint, the aromatic hydrocarbons could be considered as toxic (carcinogenic and mutagenic) at low concentrations and undesirable from a taste standpoint at much lower concentrations while the saturated hydrocarbons are considered benign but from the correlation standpoint, the quantitation of the saturated hydrocarbons is essential as the major part of the hydrocarbon in petroleum is saturated.

Therefore, an analytical scheme for the improvement of the quantity of recoverable aromatic and saturated hydrocarbons in sediment is necessary for a more valid assessment of the levels of these hydrocarbons in environmental media. Although interest is growing in frontal analysis, a sorption technique either by liquid – liquid chromatography or liquid – solid [4] but owing to the dearth of instruments and cost for such analysis presently in Nigeria, a classical scheme on column chromatography is re-appraised and better explored using the sediments from Ethiope River.

Materials and Methods
Description of the study area
The Ethiope river is located in the western part of Delta State of Nigeria and is situated between latitude 5.53° and 6.05° North and longitude 5.30° and 6.05° East. It takes its source from Umuaja in Ndokwa L.G.A of Delta State and covers a distance of 96.6 kilometres and flows into the Atlantic ocean through the Benin river. Umuaja, Umutu,obi – Iloh, Ebedei-Ukwale, Owa-Abbi, Obinomba, Obiaruku, Umeghe, Urhuoka, Abraka, Ajalomi, Urhuovie, Erho,Oria, Sanubi, Eku, Igun, Okpara Waterside, Ekpan-Ovu, Aghaiokpe,
Arabga-Okpe, Adarweran, Egbeku, Ibada, Eko, Amukpe, Okirigwhre, Sapele, Jesse, Oghara are communities traversed by the Ethiope river[5].

Fig.1: Map of Delta State showing sample locations within Ethiope River

**Sampling**

Sediment samples were collected with Van Veen grab sampler from four stations in River Ethiope(Fig. 1)

**Precautions**

The following precautions were taken in order to preserve the integrity of the samples, prevent their contamination during analysis and ensure valid conclusions.

All the organic solvents were re-distilled at least twice and solvent purity checked by boiling point determination. Only glass wares were used and effort was made not to get the extracts in contact with any rubber or plastic materials. Adsorbents were activated before another column is prepared in order to make the activity of the adsorbent constant.

Replicate analyses were carried out to check the effect of incomplete removal of solvent (if any) before gravimetric measurement.

**Sediment extraction**

The sediments were air-dried in the laboratory. Thereafter, they were pulverized and sieved through 200mesh (40nm) sieve. The sieved sample added to the soxhlet extractor was extracted with chloroform–methanol (3:1 v/v) for 48 hours [6]. Elemental sulphur was removed with activated copper turnings [7]. The extracts were collected in pre-weighted flasks. After the evaporation of the solvent, the extracts were quantified by weight difference.

**Column chromatography**

The extracts were de-asphalted by the method of [8] and [9] by precipitation in a mixture of dichloromethane–petroleum ether (B.P. 40-60°C at 1:30 v/v ratio in a centrifuge at 3,000rpm for about 20 minutes. Silica gel was activated. The silica gel was activated for 6hrs at 400°C and the neutral alumina (80-200 mesh) activated for 16 hours at 265°C[10].

Ten columns (0.65cm id x35cm long) were packed with activated alumina and silica gel (adsorbent) in different ratios by column length (Table 1) and adsorbent weight (Table 2).

The component of the adsorbent (stationary phase) packed at the bottom is written first. For SA, silica gel, S was at the bottom while alumina, A was on top and for AS, alumina was packed at the bottom while silica gel was on top. For the modified SA (MSA), silica gel was packed at the bottom, alumina in the middle and silica gel on top i.e. SAS. Thus MSA (2:1) i.e. SAS1:1:1. For the modified AS (MAS) alumina was packed at the bottom, silica gel in the middle and alumina on top, i.e. ASA. So, MAS (2:1) is ASA 1:1:1.

The column length was measured from the top of the glass wool base of the column. The column weight ratio was determined using the weight of silica gel and alumina that would give about the same column height as in column length ratio. For example, if SA(2:1) is 10g of silica gel to 5g of alumina and vice versa; SA1:1 implies 7.5g of silica gel to 7.5g of alumina.
The columns were washed with n-hexane (25mls) before chromatographic separation of samples were carried out. The de-asphaltened extracts were re-dissolved in a little quantity of n-hexane. 0.1g of the extract was applied to the top of the columns. 50ml of n-hexane solvent was used to elute the saturated hydrocarbons. The column was then flushed with another batch of n-hexane (25mls) and the eluent examined spectrophotometrically (uv – vis. Camag universal – uv lampe 29200) to ensure there was no absorption.

For the aromatic hydrocarbons, toluene was employed as the eluting solvent (50mls). The column was also flushed with another batch of toluene (25mls) and the eluent examined spectrophotometrically to ensure the complete removal of the recoverable aromatic hydrocarbons from the adsorbent. In all cases, where there appeared to be different bands in the first eluent or the eluent from the flush, a re-separation was done. The eluents were collected in pre-weighed flasks. After the evaporation of the solvents, the fractions were quantified by weight difference. The weights of the fractions were expressed in parts per million (ppm) or microgram per gram (μg/g) of the sediment weight.

Table 1: Concentrations of saturated and aromatic hydrocarbons (Column length ratio)

<table>
<thead>
<tr>
<th>S/N</th>
<th>Column length ratio</th>
<th>SHC (PPM)</th>
<th>ARO(PPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
<td>II</td>
<td>III</td>
</tr>
<tr>
<td>1.</td>
<td>SA(1:1)[11]</td>
<td>99</td>
<td>106</td>
</tr>
<tr>
<td>2.</td>
<td>SA(2:1) [12]</td>
<td>287</td>
<td>347</td>
</tr>
<tr>
<td>3.</td>
<td>SA(1:2)</td>
<td>113</td>
<td>124.4</td>
</tr>
<tr>
<td>4.</td>
<td>AS(1:1)</td>
<td>67</td>
<td>81</td>
</tr>
<tr>
<td>5.</td>
<td>AS(2:1)</td>
<td>75</td>
<td>89</td>
</tr>
<tr>
<td>6.</td>
<td>AS(1:2)</td>
<td>74</td>
<td>88</td>
</tr>
<tr>
<td>7.</td>
<td>S</td>
<td>66</td>
<td>68</td>
</tr>
<tr>
<td>8.</td>
<td>A</td>
<td>30</td>
<td>106</td>
</tr>
<tr>
<td>9.</td>
<td>MSA(2:1)</td>
<td>29</td>
<td>43</td>
</tr>
</tbody>
</table>

Table 2: Concentrations of saturated and aromatic hydrocarbons (Column weight ratio)

<table>
<thead>
<tr>
<th>S/N</th>
<th>Column length ratio</th>
<th>SHC (PPM)</th>
<th>ARO(PPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
<td>II</td>
<td>III</td>
</tr>
<tr>
<td>1.</td>
<td>SA(1:1)[10]</td>
<td>79</td>
<td>98</td>
</tr>
<tr>
<td>2.</td>
<td>SA(2:1)</td>
<td>7</td>
<td>49</td>
</tr>
<tr>
<td>3.</td>
<td>SA(1:2)</td>
<td>39</td>
<td>49.5</td>
</tr>
<tr>
<td>4.</td>
<td>AS(1:1)</td>
<td>35.5</td>
<td>29</td>
</tr>
<tr>
<td>5.</td>
<td>AS(2:1)</td>
<td>78</td>
<td>99</td>
</tr>
<tr>
<td>6.</td>
<td>AS(1:2)</td>
<td>65</td>
<td>75</td>
</tr>
<tr>
<td>7.</td>
<td>MSA(2:1)</td>
<td>79.9</td>
<td>73</td>
</tr>
<tr>
<td>8.</td>
<td>MAS(2:1)</td>
<td>22.9</td>
<td>19</td>
</tr>
</tbody>
</table>

**Column length ratio**

In table 1, no. 3, the composition SA (1:2) column length ratio gave the highest concentration of saturated hydrocarbons from sediments I, II, III and IV. However, its aromatic hydrocarbon yields ranked 5th of the ten compositions by column length under investigation. No. 9, MSA (2:1) eluted the highest concentration of aromatic hydrocarbons from sediments I, II, III and IV. This suggests that the relative elution of the saturated and aromatic hydrocarbons is differently influenced by the composition of the column packing. The yields of the aromatic and saturated hydrocarbons relative to the
column packing are due to the differences in the relative adsorption of the aromatic and saturated hydrocarbons on the stationary phase and the moderating influence of the components of the stationary phase on each other. The saturated hydrocarbons do not adsorb well on the alumina relative to the silica gel due to polarity difference. Therefore, descending the comparatively longer length of the alumina (SA1:2) with the bulk of the mobile phase preserves its local concentration and enhances its recovery.

In no.9, MSA (2:1) i.e. SAS (1:1:1), the enhanced recovery of the aromatic hydrocarbons may be as a result of the first contact of the aromatic hydrocarbon with silica gel on which it has lower adsorptivity. As a result of adhesion on alumina the elution rate is retarded making way for a dispersion interaction with the alumina layer before finally getting to the last layer of the silica gel.

No.1, SA (1:1) and no.4, AS (1:1) are of the same column length ratio but of different order of packing. While in SA (1:1) more aromatic hydrocarbons were obtained; in AS (1:1) more saturated hydrocarbons were obtained. It does appear here that the momentary hold of the aromatic hydrocarbons by the alumina layer due to polarity similarity and the consequence dispersion interaction enhanced the aromatic hydrocarbon elution in SA (1:1). In AS (1:1), the momentary hold of the saturated hydrocarbons on silica gel due to the same reasons added above enhanced their elution. However, the same did not hold for no.2, SA (2:1) and no.5, AS (2:1). This is possibly due to the differences in the heights of the silica gel and alumina in each case unlike the no. 1, SA (1:1) and no. 4, AS (1:1).

No. 10, MAS (2:1) eluted the lowest concentration of the saturated and aromatic hydrocarbons. This suggests that having alumina at the bottom and at the top with silica gel in between, ASA (1:1:1) immensely disrupts the dispersion interaction of the saturated and aromatic hydrocarbons. Consequently, their concentrations are respectively reduced.

A preliminary look at table 1 shows that the differences in the concentrations of the respective hydrocarbons are appreciable especially the aromatic hydrocarbons which at very low concentration (few nanograms per kilogram) are considered toxic.

The statistical treatment of the data using t-test at 0.05 confidence level and 5 degrees of freedom shows that a significant difference exists between the aromatic hydrocarbon concentrations obtained from the column length ratios, SA (2:1) and MSA (2:1), no. 2 and no.9 respectively (t-calculated = 4.03 and t-critical = 2.78). For no.1, SA(1:1) and no.4, AS(1:1); no.5, AS(2:1) and no.9, MAS(2:1); no.2, SA(2:1) and no.3, SA(1:2) there were no significant differences in the aromatic hydrocarbon concentrations obtained from them as the calculated t-values(1.82, 1.01 and 0.60) are less than the critical value of t, 2.78.

No. 5, AS(2:1) and no.10, MAS(2:1); no.2, SA(2:1) and no.3, SA(1:2), showed significant differences in the saturated hydrocarbon concentrations obtained from them as the values of the calculated t are 5.2 and 7.5 respectively against the critical value of t, 2.78.

**Weight ratio**

In table 2, no. 1, SA (1:1) eluted the highest amount of saturated hydrocarbons. No. 5, AS (2:1) eluted the highest amount of aromatic hydrocarbons. These are different from those of the column packings that eluted the highest amounts of saturated and aromatic hydrocarbons in the column length ratio.

No. 8, MAS (2:1) eluted the lowest amount of saturated hydrocarbons as in column length ratio while no.1, SA (1:1) eluted the lowest amount of aromatic hydrocarbons.

A cursory look at table 2 shows that a noticeable difference exists in the concentration of the aromatic and saturated hydrocarbons. No. 1, SA (1:1) and no. 5, AS (2:1); no.5, AS (2:1) and no. 8, MAS (2:1) weight ratios exhibited significant differences in the concentrations of the aromatic hydrocarbons obtained from them, t-calculated, 4.11 and 2.94 respectively are higher than the value of t-critical, 2.78.

For the saturated hydrocarbon, no. 5, AS (2:1) and no. 8, MAS (2:1), there was a significant difference between them (t-calculated = 7.53) but no. 1, SA (1:1) and no. 5, AS (2:1); no. 2, SA (2:1) and no. 7, MSA(2:1) showed no significant differences (t-calculated = 0.46 and 2.03 respectively).

On a comparative note, the packing by column length ratio eluted higher amounts of aromatic and saturated hydrocarbons than the packings by weight ratio. MSA (2:1) eluted the highest mean concentration of aromatic hydrocarbon in column length ratio (110.5±18ppm) and AS (2:1) eluted the highest mean concentration of aromatic hydrocarbons in column weight ratio (49.3±13.6ppm). The calculated t-value of 2.81 for the two column packings showed a significant difference in the eluted aromatic hydrocarbon concentrations.

Similarly, SA (1:2) column length ratio eluted the highest mean concentration of saturated hydrocarbon in column length ratio (322.75±8.5ppm) while SA (1:1) eluted the highest mean concentration of saturated hydrocarbon in column weight ratio (98.3±20.6ppm). The calculated t-value of 3.63 for the column packings showed a significant difference in the eluted amount of saturated hydrocarbon concentrations.

However, there were few cases where the column packing by weight ratio eluted higher amounts of aromatic hydrocarbons [SA(2:1); MAS(2:1)] and saturated hydrocarbon [SA(1:1); AS(2:1); MSA(2:1)], but statistically there were no significant differences in the aromatic and saturated hydrocarbon concentrations.
between them and their column length ratio equivalents. For example the t-value for the aromatic hydrocarbon concentrations for SA (2:1) weight ratio and SA (2:1) column length ratio is 0.44 against the critical t-value of 2.78. Similarly, the t-value for the saturated hydrocarbon concentrations for SA (1:1) weight ratio and SA (1:1) column length ratio is 0.32 against the critical t-value of 2.78.

Conclusion
In column chromatographic separation, the modification of the column packing by column length ratio and weight ratio influence the concentrations of the saturated and aromatic hydrocarbons recovered. Comparatively, the column packing by column length ratio eluted more saturated and aromatic hydrocarbons than the column packing by weight ratio and the maximum concentrations of aromatic and saturated hydrocarbons were given by different column packings by column length ratio. For aromatic hydrocarbons, MSA (2:1) and saturated hydrocarbons, SA (1:2).

Acknowledgment
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References